IITRI-B6049-12
(Final Report)

# STUDY OF FACTORS AFFECTING CHEMICAL MILLING

National Aeronautics & Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

Contract No. NAS 8-20112

IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

IITRI Project No. B6049

# STUDY OF FACTORS AFFECTING CHEMICAL MILLING

IITRI-B6049-12
(Final Report)

June 1, 1965 to June 1, 1966

Prepared by:

Howard T. Francis

Prepared for:

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

Contract No. NAS 8-20112

June 30, 1966

## STUDY OF FACTORS AFFECTING CHEMICAL MILLING

### ABSTRACT


A study has been made of the chemical milling characteristics of certain aluminum alloys: Types 2219, 2014, 5456, and 7075. The cause of nonuniform stock removal for Type 2219, the relation between stretch marks and milling uniformity for Type 5456, and the causes of rough etching in Types 2014 and 7075 were investigated.

The results in brief are:

(1) The difficulties with 2219 are caused by nonuniform quenching after solution treatment; the recommended corrective measure is to quench "chem-milling grade Type 2219" by total immersion in water, rather than by spray quenching.

(2) The stretch marks in Type 5456 do not affect chem-milling at all; if they must be avoided, it must be by prevention of their formation in the first place, since they are not removed during milling.

(3) The roughness met in chem-milling Type 2014 is primarily associated with its "naturally aged" temper (T4). However, there is apparently a composition-dependent effect, as well. The recommended corrective measures are: (a) to chem-mill this alloy only in the artificially aged condition (T6), or (b) to develop a special grade of Type 2014 alloy that mills satisfactorily in the T4 temper.

(4) The roughness occasionally met in chem-milling Type 7075 alloy is truly a "random" effect and is probably determined by the chemical composition of the alloy (not by heat-treatment variables). The corrective measures must, therefore, be centered on developing a special "milling-grade" alloy.

## TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

## LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (continued)

## LIST OF ILLUSTRATIONS (continued)

# STUDY OF FACTORS AFFECTING CHEMICAL MILLING

## I. INTRODUCTION

The extreme size and the severe strength and weight requirements of space vehicles demand the use of unconventional metal fabrication techniques. One of these is the technique of "Chem-Milling,"* in which heavy plates are converted to lightweight, integrally-stiffened components by chemical dissolution of metal from selected (unmasked) areas. The remaining (masked) zones are unattacked and form the reinforcing ribs. This technique has been used chiefly on large, unwieldy, precurved sections of high-strength aluminum alloy plate. A typical component is a gore section for the bulkhead of a booster tank.

The chemical milling method has a number of advantages over mechanical methods, the most notable being the simplicity of the equipment required. In the early part of the rocket booster development program, the extremely large and complex machines required for mechanical milling did not exist, hence the chem-milling approach was adopted. More recently, however, the techniques of numerical programming have been applied to the milling of complex sections, so that chemical milling is no longer the only practical fabrication method for such components.

The present program has been directed toward obtaining a better understanding of the relation between metallurgical processing variables and the chem-milling characteristics of four specific aluminum alloys: Types 2219, 5456, 2014, and 7075. More particularly, certain heat treatments and certain tempers of these alloys give difficulty in the form of rough milling or nonuniform removal of stock. Through chem-milling

*"Chem-Mill" is a trade name owned by North American Aviation, Inc., and licensed to Turco Products, Inc.

experiments on laboratory-prepared alloy specimens, the effects of quenching rate, cold work, stretch marks, aging practice, and similar variables have been correlated with the chem-milling qualities of the alloys.

In this report, the experimental results and their interpretation will be presented separately for each type of alloy, after a brief general discussion of the essential principles of chemical milling.

## II. THE ELECTROCHEMISTRY OF CHEMICAL MILLING

When pure aluminum is placed in hot, concentrated sodium hydroxide solution, a vigorous reaction occurs and the metal dissolves rapidly in accord with the reaction:

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow \qquad (1)$$

This reaction is very similar to the familiar attack of a metal by acid, such as iron dissolving in hydrochloric acid:

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2\uparrow \qquad (2)$$

These reactions are so vigorous and produce such general attack on the metal surface that it is tempting to consider them "chemical" reactions rather than "electrochemical" reactions. They are, however, electrochemical in nature, a fact that becomes clear when certain alloys are observed to suffer quite nonuniform attack in sodium hydroxide.

To clarify this point, let us consider the reaction between aluminum and aqueous sodium hydroxide in more detail. The metallic aluminum (valence of zero) is converted to aluminum ion in accord with the oxidation reaction:

$$Al^{o} \longrightarrow Al^{+++} + 3e \qquad (3)$$

The hydrogen of the water (valence of 1) is converted to hydrogen gas (valence of zero) in accord with the reduction reaction:

$$H_2O + e \longrightarrow OH^- + 1/2\ H_2\uparrow \qquad (4)$$

These two reactions occur at the "anode" and the "cathode," respectively, of an electrochemical cell, the over-all reaction--in the presence of NaOH--being reaction (1). If these reactions occur in very close proximity to each other on the metal surface, the attack will be uniform and we will observe a "smooth milling" specimen. If, however, the anodic (dissolved) regions are widely dispersed, we will see the development of "roughness," since the cathodic reaction does not result in metal removal.

Now, the problem is to learn just what metallurgical and chemical conditions lead to large and wide-spread cell elements and, hence, to roughness in the chem-milled surface.

Certainly the milling characteristics are related to the metallurgical composition and structure of the alloy. The question, however, is to determine how the relatively <u>fine</u> structure of the metal can be related to the rather <u>coarse</u> nature of a rough-milled aluminum surface. In other words, the roughness of a milled specimen is dimensionally many times larger than the "unit cell" of the alloy structure; or, put another way, if the anodes and cathodes of the dissolution reaction were distributed in the same way as the structural particles of the alloy, the chemical attack would still be much finer than that actually observed.

If there is no direct correspondence between the structural features of the alloy and the actual "high" and "low" spots on the milled metal, then what <u>does</u> cause one alloy to mill smoothly and another to develop an irregular surface? We shall examine this question again after presenting the experimental results for each of the alloys considered.

The specific problems investigated were these:

1. Type 2219-T37 alloy frequently shows nonuniform stock removal over the area of a large plate. These variations are quite gross compared to the microstructure of the alloy.
2. Type 5456 alloy shows stretch marks when fabricated; the influence of these marks on the uniformity of subsequent chem-milling is not entirely clear.
3. Type 2014 alloy in the naturally aged condition (T451) shows rough surface finish, whereas in the artificially aged condition (T651) it yields a smooth surface.
4. Type 7075 alloy frequently shows rough surfaces when milled, for reasons that are not understood.

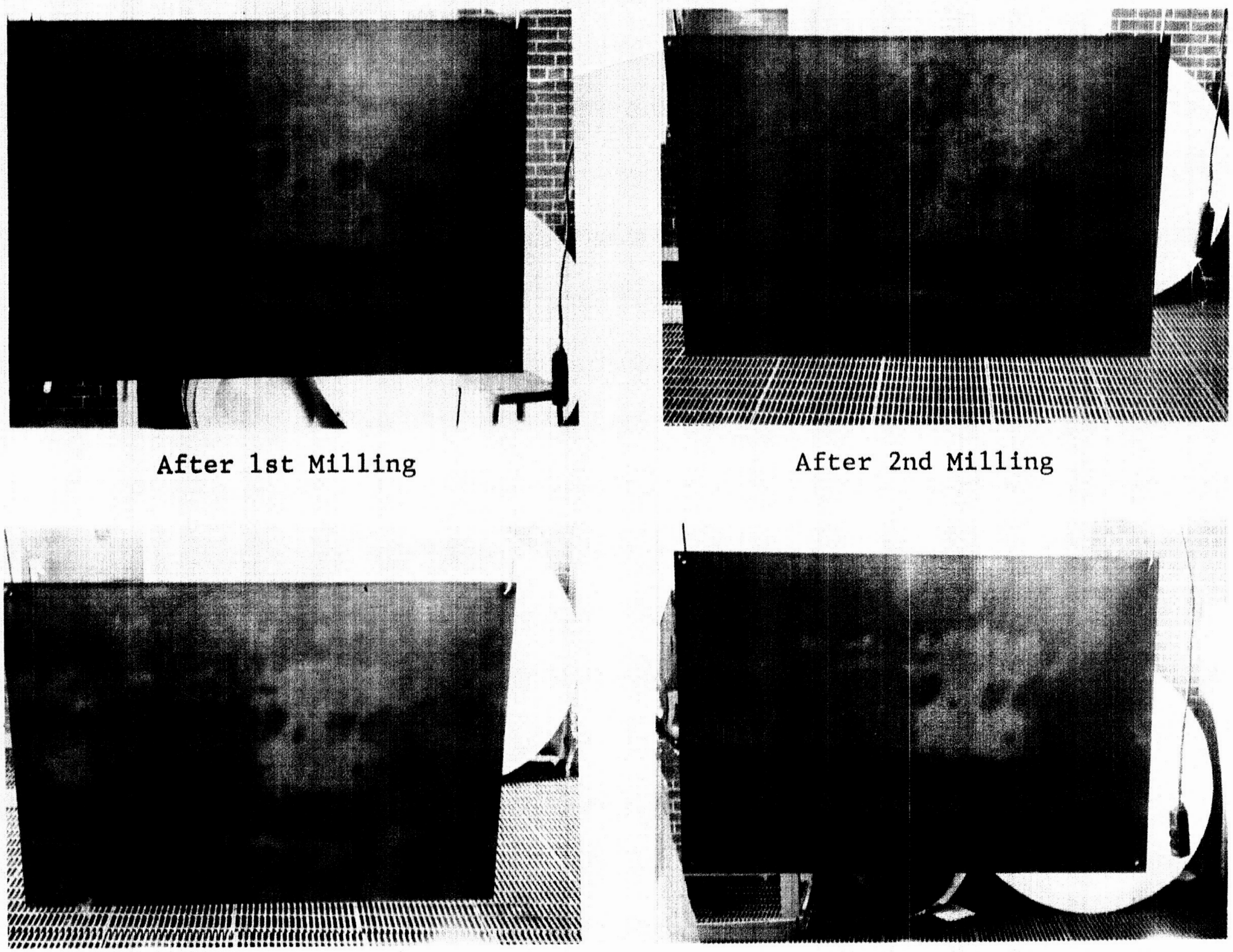
## III. STUDIES OF TYPE 2219 ALUMINUM

### A. Nonuniform Stock Removal

The problem posed by Type 2219 alloy can best be described by reference to the photographs* of Figure 1-A. A 2 in. thick plate of Type 2219-T37 alloy was chemically milled several times and photographed at each stage. A persistent pattern of nonuniform attack was visible at each stage, showing that the metallurgical factors responsible for the nonuniform attack penetrate the plate transversely--at least part way through the thickness. In Figure 1-B the opposite face of the plate is shown at three different steps in the milling treatment. Again, although the pattern is not identical on the two faces, the similarity is great enough to suggest that they have a common origin.

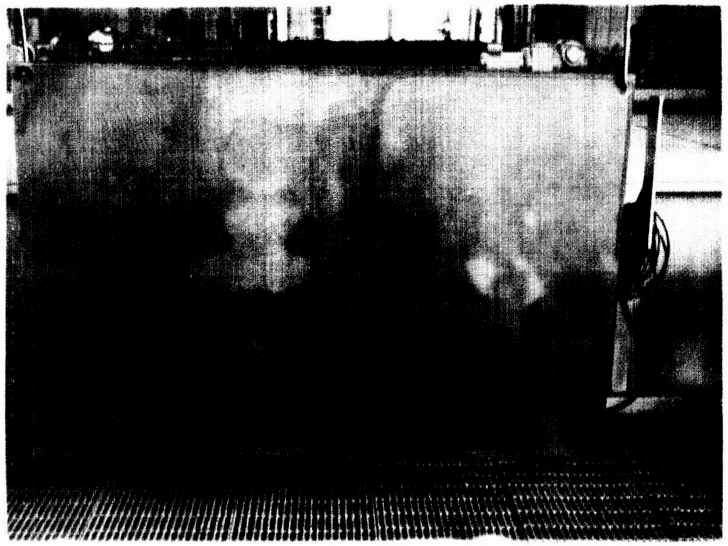
---

*Photographs made by the Manufacturing Engineering Laboratory, George C. Marshall Space Flight Center, August 12, 1963.

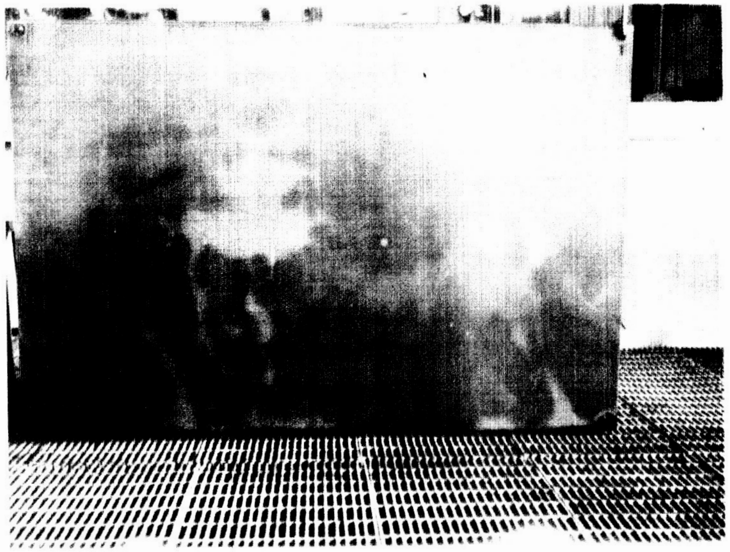


After 1st Milling — After 2nd Milling — After 3rd Milling — After 4th Milling

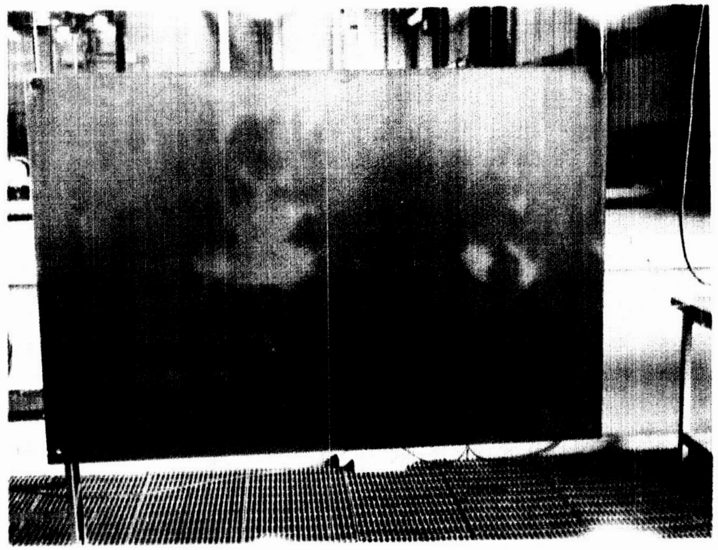
Fig. 1-A - Side "A" of Type 2219-T37 Aluminum Plate (48 x 72 x 2 in). Note Persistence of Pattern Through Four Successive Chem-Milling Steps.



After 2nd Milling



After 3rd Milling



After 4th Milling

Fig. 1-B - Side "B" of Plate Shown in Figure 1-A. Note Similarity of Pattern on Opposite Sides of Plate.

B. Quench Rate Experiments

The general appearance of the plate in Figure 1 and similar other specimens strongly suggests that the patterns have their origin in the quenching practice used on the product. In an earlier program (Contract No. NAS 8-11444, entitled "Investigation of Random Thickness Variations in Chem-Milled 2219-T37 Aluminum Alloy"), it was determined that when a bar was quenched along only part of its length, milling was much more rapid in the "air-cooled" region than in the "water-quenched" region. Accordingly, it was considered desirable in the present program to make a much more thorough study of such quenching effects.

1. Cooling Rate Variations

One inch square samples of Type 2219-T37 aluminum were cut from 0.4 in. thick plate. A hole was drilled in one edge of each specimen, extending to the center of the piece. A Chromel-Alumel thermocouple was fitted into this hole and wedged in place with a small aluminum plug, as shown in Figure 2.

A number of such specimens were placed in a furnace at 990°-1000°F (the nominal solution-treatment temperature for Type 2219) for 2 hr, then quenched in water at various temperatures and periods of time. The temperature-time curve for each specimen was recorded on a Speed-O-Max recorder.

Representative cooling curves are shown in Figure 3 for three progressively less severe quenching treatments. The difference in cooling rate for a specimen plunged into water at 25°C (77°F) and one immersed in boiling water is very striking. Of course, air cooling is even slower, as would be expected. The approximate cooling rates measured in the experiments described here are:

| | | |
|---|---|---|
| Water at 25°C (77°F) | - | 500°F/sec |
| Boiling water | - | 23°F/sec |
| Air | - | 1°F/sec |

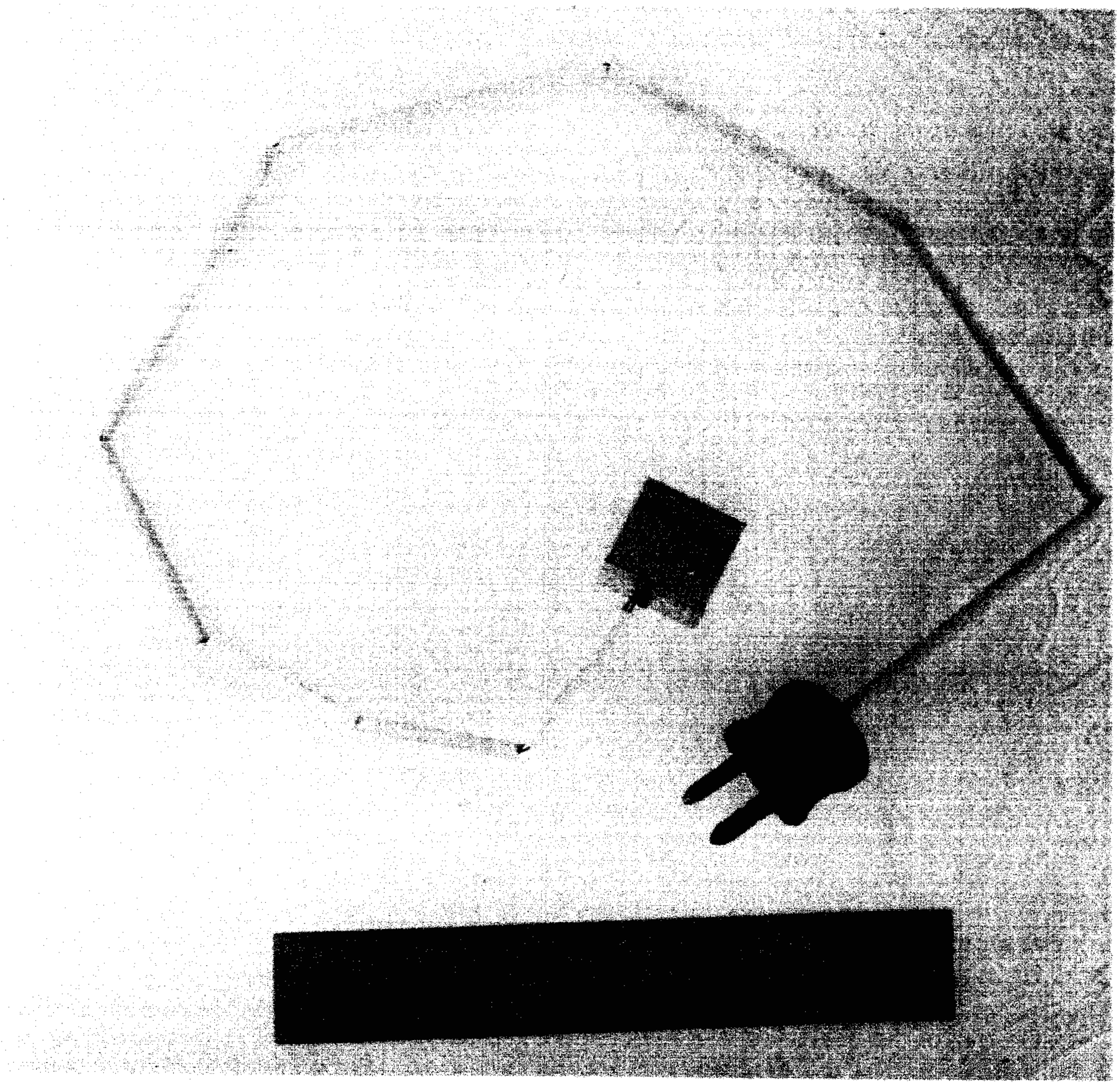


Fig. 2 - Specimen Used in Quench-Rate Studies on Type 2219 Aluminum.

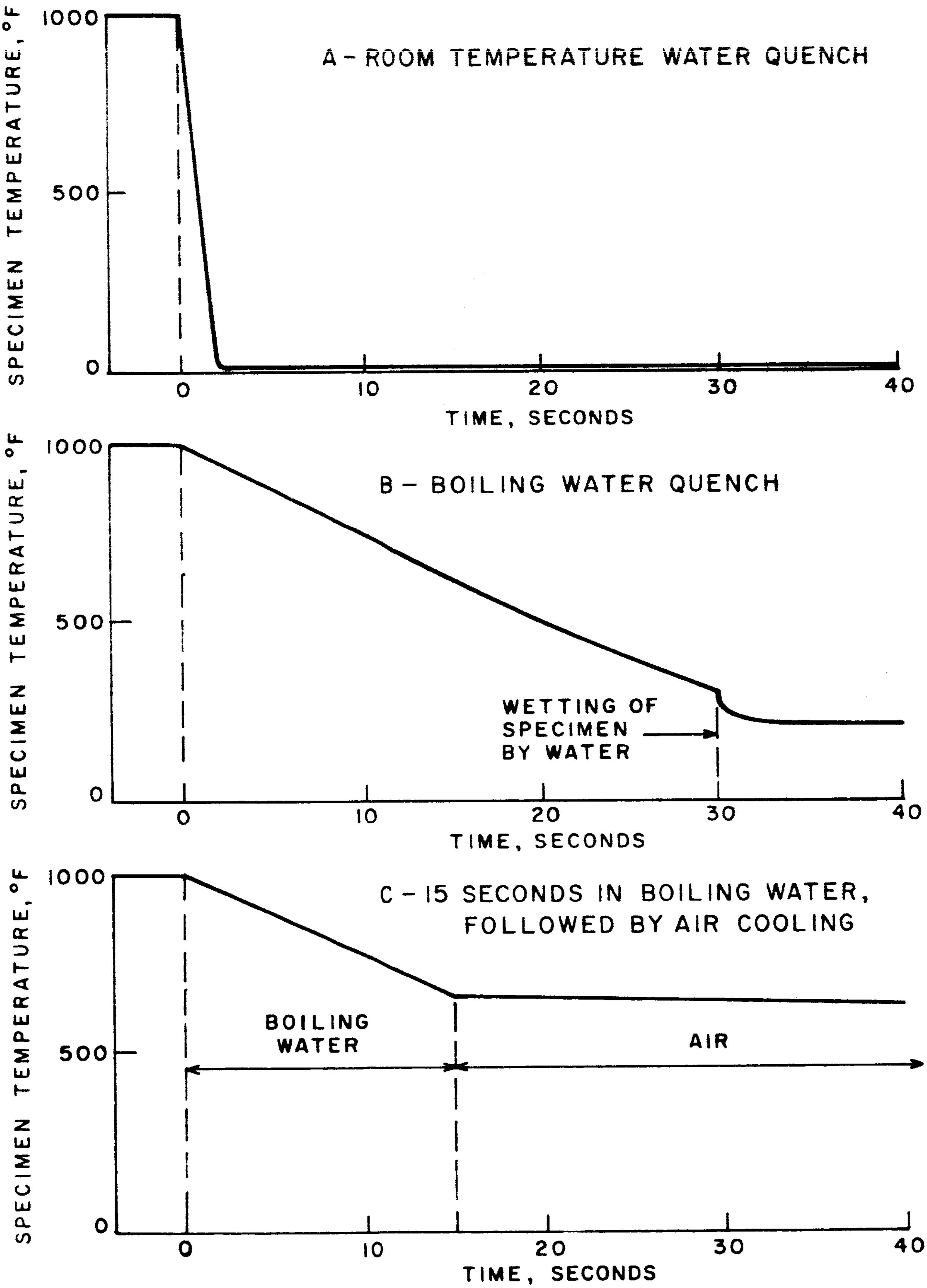



Fig. 3 - Cooling Curves for Various Quenching Conditions. All specimens quenched from 1000°F at time zero.

It should be noted (Figure 3) that when a hot specimen is immersed in boiling water, no wetting occurs until the specimen has cooled nearly to the water temperature. Thus, heat extraction occurs only through a steam blanket, and is considerably slower than in cold water.

## 2. Etch Rate Measurements

Using the quenching technique just described, a large number of specimens were prepared. Cooling rates varied from air-cooling to quenching in ice water at 0°C (32°F). In order to cover the range of cooling rates between air cooling and a boiling water quench, specimens were immersed for various times between 0 and 25 sec in boiling water, followed by air cooling to room temperature. For more severe quench treatments, the water temperature was varied between 100°C (212°F) and 0°C (32°F).

These specimens were then subjected to chemical milling under standardized conditions of time, composition, and temperature, as follows:

NaOH - 15 oz/gal.
Temperature - 190°F
Time - 30 min

Five specimens were milled simultaneously and fresh solution used for each group so that all specimens received essentially identical treatment. The results are shown in Figure 4. The maximum in the curve indicates that a considerably higher milling rate would be expected in an area of a plate that had been covered with a steam blanket during quenching.

These results were duplicated very closely in another group of specimens run under slightly different milling conditions. In this series, the quenching treatments were the same as described above, but the temperature of the NaOH solution was somewhat higher, resulting in a slightly higher etch rate for

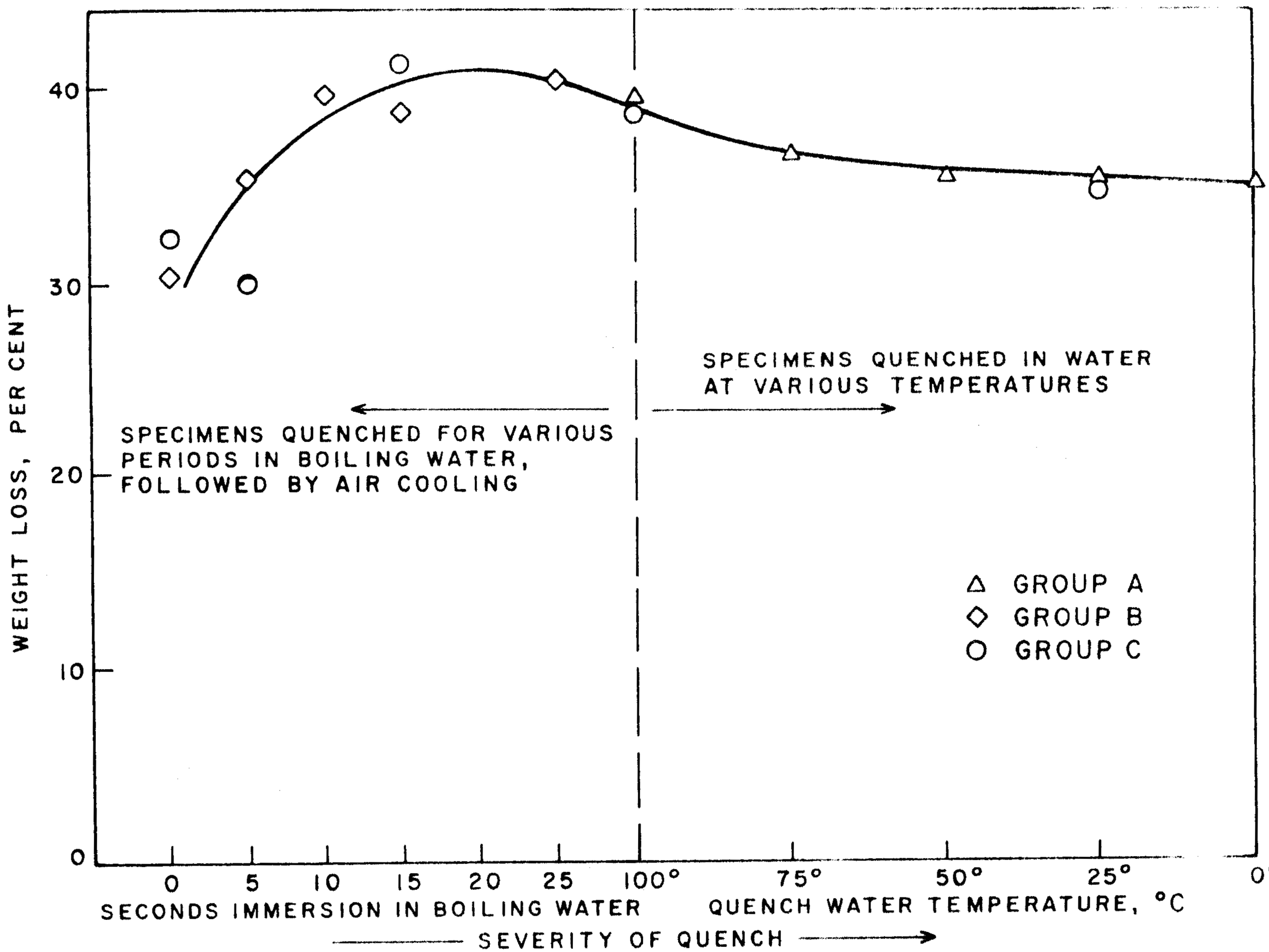



Fig. 4 - Effect of Quench Rate on The Rate of Chemical Milling of Type 2219 Aluminum.

all specimens. The results are shown in Figure 5. The maximum in the curve is at approximately the same "severity of quench" as in Figure 4.

Milling rates were measured in several other media, with the results shown in Table I. It is clear that the differences due to quenching observed in NaOH are present to about the same degree in the other alkaline media. The effect of quenching is also noted in ferric chloride solutions, and becomes quite dramatic in dilute HCl, where attack was quite slow except at the grain boundaries of the material quenched in boiling water. Here the aluminum was actually not attacked as severely as the weight loss would indicate; most of the aluminum was converted to fine powder (actually individual grains) that simply fell away from the specimen.

### 3. Electrode Potential Measurements

In the hope that further light might be cast on the observed relation between quench rate and milling rate for Type 2219 alloy, a series of potential measurements were made on specimens during actual chem-milling runs. Since the conditions that obtain during chemical milling are certainly not "reversible" in the thermodynamic sense, these data are more properly termed "corrosion" or "dissolution" potentials. This expression takes account of the fact that both anodic and cathodic reactions are proceeding at extremely rapid rates and the measured potential is the "polarized half-cell potential" for both the anodic and cathodic elements of the (vigorously) corroding couple. Such measurements in no way "explain" the behavior of the specimen, but may often be interpreted in the light of the metallurgical data that are also available.

This experiment was essentially the same as those summarized in Figures 4 and 5. The weight loss data were simply paralleled by potential measurements, against a nickel-nickel

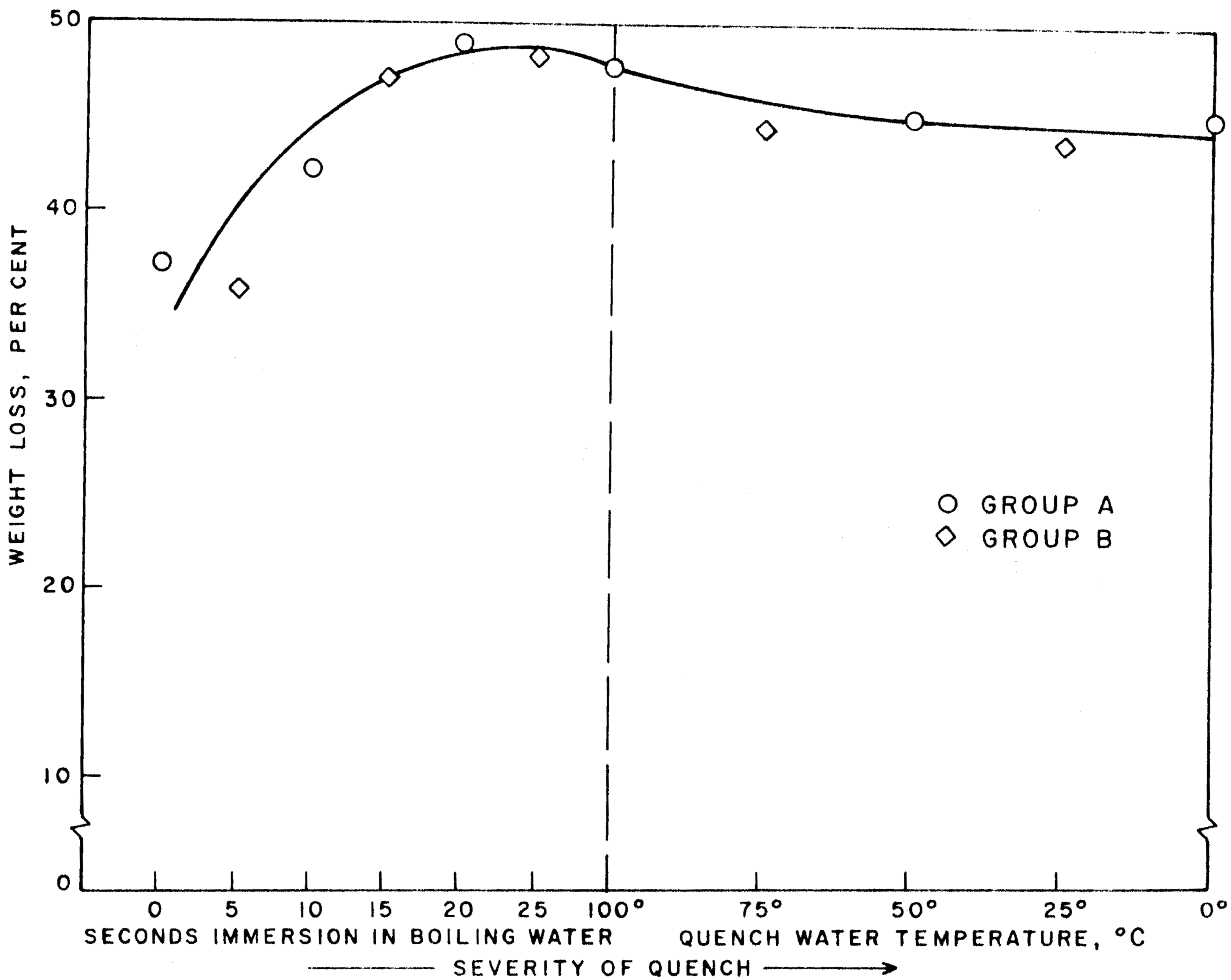



Fig. 5 - Effect of Quench Rate on Milling Rate.
(Confirmation of Figure 4; See text).

TABLE I

MILLING RATES IN VARIOUS MEDIA

(Type 2219 aluminum, solution treated 2 hr at 990°-1000°F, quenched in water.)

| Etchant | Etching Condition | Weight Loss, % Quenched in Boiling Water | Weight Loss, % Quenched in Water at 25°C |
|---|---|---|---|
| Sodium Hydroxide | 15 oz/gal, 190°F, 30 min | 39.0 | 35.0 |
| Turco 13 | 190°F, 30 min | 22.9 | 20.3 |
| Wyandotte Mil-Etch | 15 oz/gal, 178°F, 30 min | 39.5 | 36.5 |
| Ferric Chloride, 5% | Not acidified, Room temp., 30 min | 17.7 | 11.7 |
| Ferric Chloride, 5% | Acidified with HCl, Room temp., 30 min | 25.8 | 16.2 |
| Hydrochloric Acid | 1% by weight; Room temp., 3 days | 21.0* | 0.5 |

*Pronounced intergranular corrosion.

oxide reference electrode, and recorded on the Speed-O-Max recorder. The results are shown in Figure 6, where once more the relation between quench severity and milling rate is confirmed.

It is most surprising to find that there is no relation whatsoever between the milling rate curve and the potential curve. The explanation probably lies in the fact that there is no direct relation between "corrosion rate" and "corrosion potential." The rate of attack on a metal is determined by the couple current that flows between local anodes and local cathodes. The potential, however, is determined by the relative areas of anodic and cathodic zones and the E vs. I curves for each of them, i.e., their "polarization" curves.

In the present case, it is obvious that the corrosion current passes through a maximum at a "quench severity" approximating immersion for 20 sec in boiling water, followed by air cooling. On one side of this point the current is evidently limited by the available cathodic areas, while on the other side the corrosion rate is limited by available anodic zones. There is no basis on which one can decide which condition obtains on which side of the milling rate maximum. However, it is reasonable to believe that on the very slow quench side the aluminum solid solution is more nearly pure aluminum--hence more anodic (more negative)--while on the rapid quench side, the solid solution is more noble--hence more positive. But this is only conjecture, and in no way contributes to the solution of the problem.

It remains that in order for Type 2219-T37 aluminum to be uniformly chem-milled in NaOH it must be uniformly quenched. The function of milling solution composition will be discussed later.

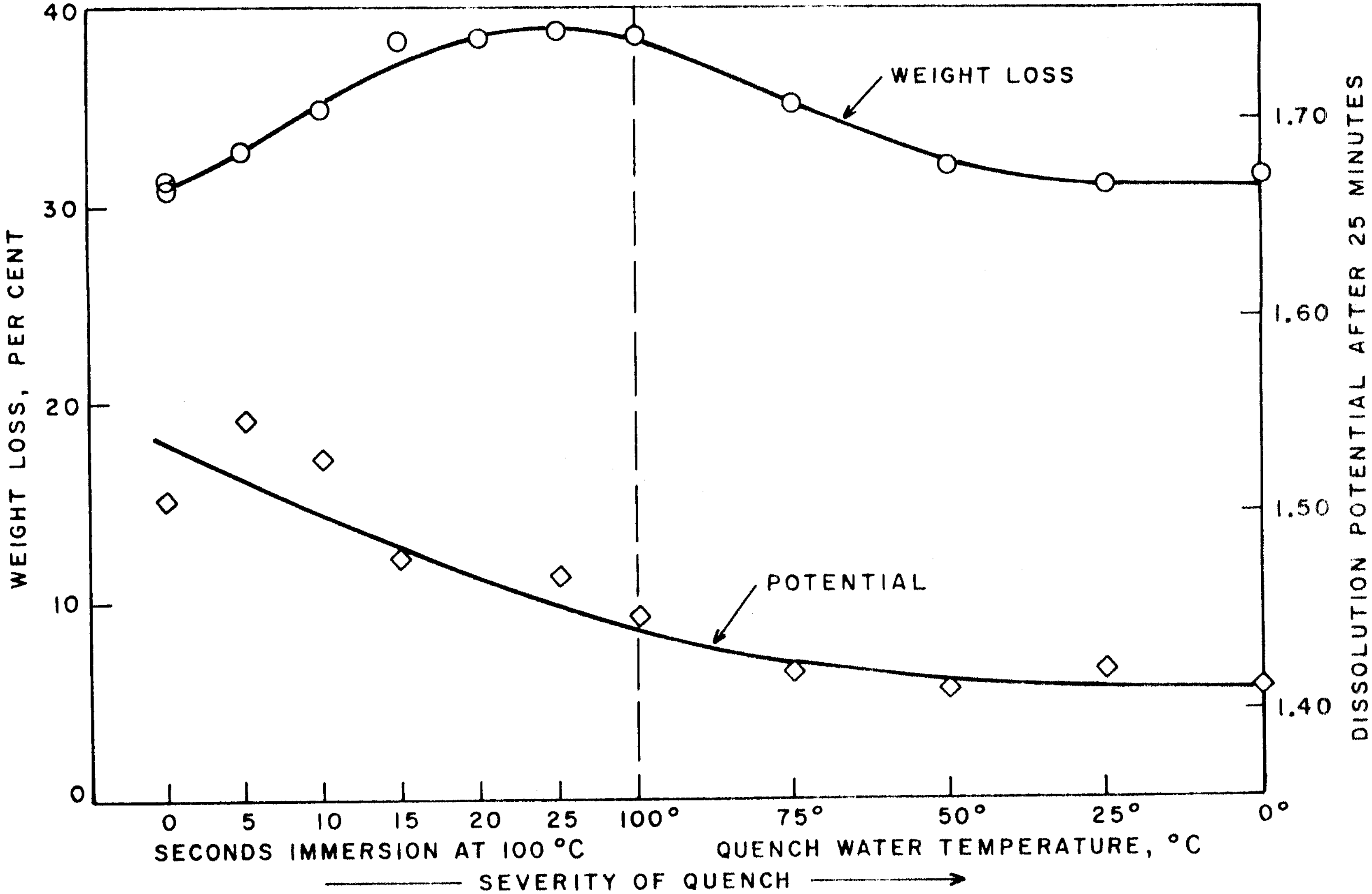



Fig. 6 - Weight Loss and Dissolution Potential for Various Quench Treatments of Type 2219 Aluminum.

## C. Effect of Cold Work

Because the manufacture of Type 2219-T37 aluminum involves a certain amount of cold work after heat treatment, it was considered desirable to investigate the possible effect of this variable on milling rate. Accordingly, a number of specimens of Type 2219 alloy were solution treated at 990°-1000°F and water quenched at 25°C (77°F). These were then subjected to simple compression in an hydraulic press to yield reductions in thickness of 0-7%. The specimens were then chem-milled in sodium hydroxide, using the same conditions as described earlier. The data are shown in Figure 7.

Although there is somewhat more scatter in the data than might be expected (based on the very good reproducibility of the quench rate vs. milling rate data) there is little doubt that the degree of cold work in Type 2219 alloy is without significant effect on the chem-milling rate.

## D. Hardness Variations

There was available for examination a sample plate of Type 2219-T37 alloy that had been chem-milled at NASA (MSC) and showed severe nonuniformity in milling rate. A typical section of this plate was removed for metallographic examination. The section selected displayed both "fast" and "slow" milling zones in close proximity. Since it is difficult to present the appearance of such regions photographically, the surface contours are given at three "scan-line" positions on the specimen; see Figure 8. The low point in the center of Scan C represents a deeply milled "valley" flanked by lightly milled "plateaus."

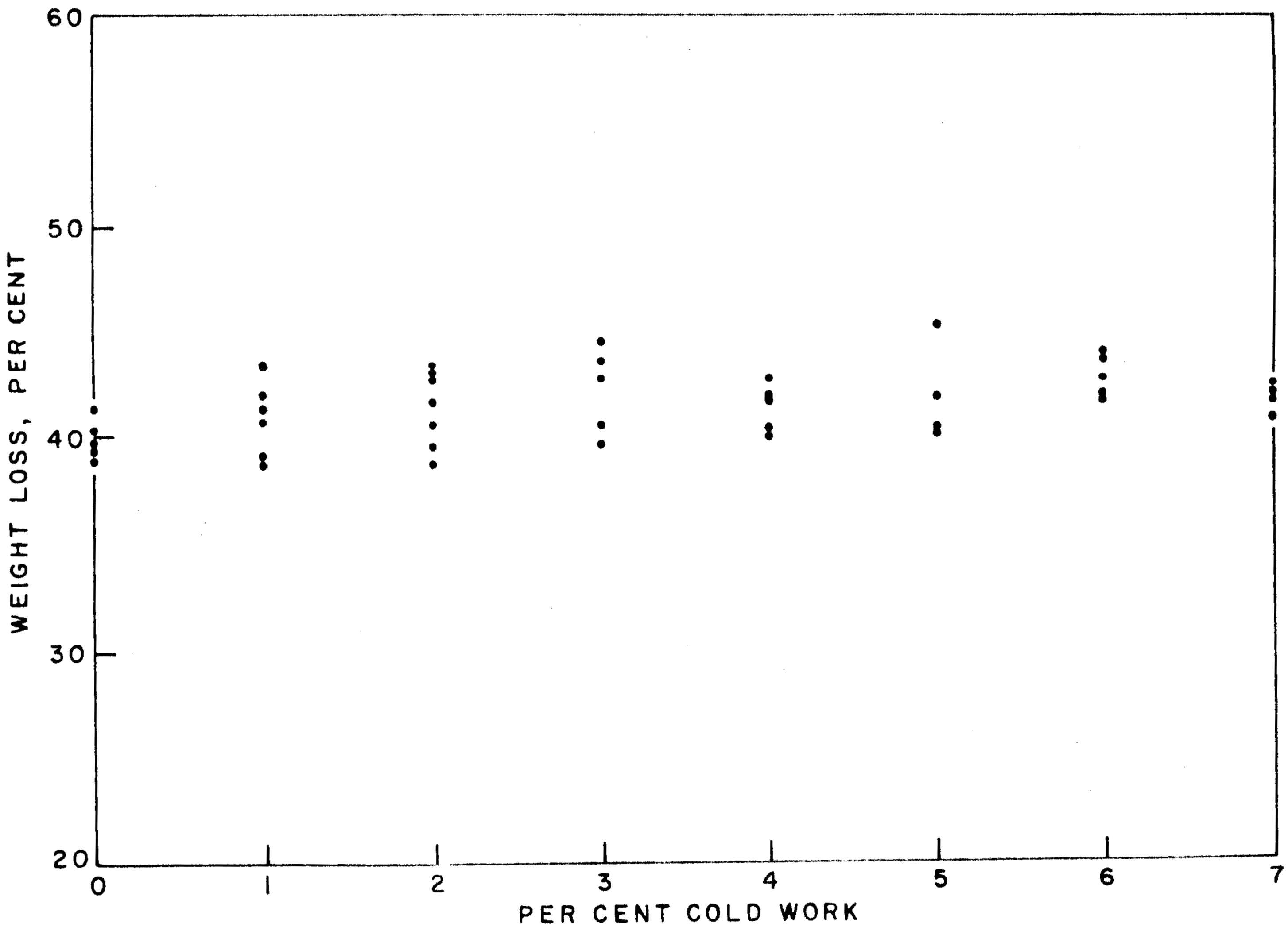



Fig. 7 - Effect of Cold Work on Milling Rate for Type 2219 Aluminum.

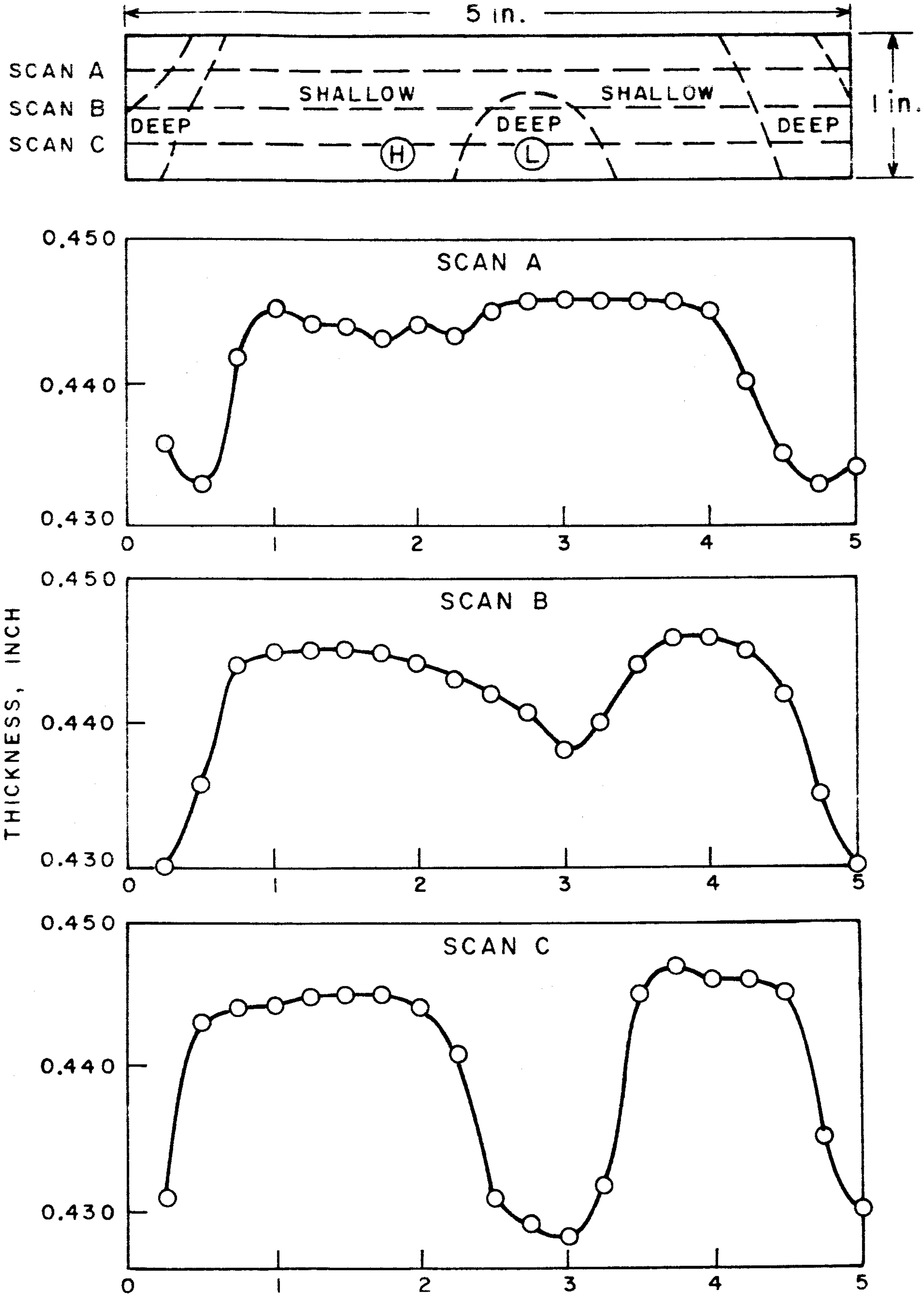



Fig. 8 - Milling Contours on Specimen of Type 2219-T37 Aluminum.

Samples were removed from the specimen at points "H" and "L" (see top of Figure 8), and hardness measurements made using a Vickers hardness tester (DPH, 5 kg load). The results were:

| | "High" region (slow milling) |
|---|---|
| | 131 |
| | 125 |
| | 127 |
| | 126 |
| | 126 |
| Average | 127 |

| | "Low" region (fast milling) |
|---|---|
| | 119 |
| | 123 |
| | 120 |
| | 115 |
| | 118 |
| Average | 119 |

These data indicate that the slower milling zones were harder than the rapidly milling areas. This result confirms the earlier indication that the more rapidly quenched areas are slower milling than the less severely quenched zones. The rapid-quench zones would be expected to be somewhat harder than the slow-quench regions, since the former would have more finely precipitated hardening constituents.

## E. Metallographic Studies

Having established the relationship between quenching treatment and milling characteristics for 2219 alloy, an attempt was made to relate quench rate to metallurgical structure. Samples of laboratory-prepared material were selected from the specimens used in Section III-B (above), as well as from the large plate discussed in Section III-D. Both optical (up to 1000X) and electron microscope (up to 48,000X) examinations were made.

Samples from the high region "H" (slow etching) and the low or fast etching region "L" of Figure 8 were mounted and examined at 250 and 1000X. The results are shown in Figures 9 and 10, at 250 and 1000X, respectively. There is not a great deal of difference evident at 250X, probably the most pronounced difference being the somewhat clearer definition of grain boundaries in the fast-etching zone. At 1000X (Figure 10) one can distinguish the greater degree of precipitation in the fast-etching specimen, as well as the precipitate-free region in certain grain boundaries. The slow-etching sample, however, shows much less general precipitation and no marked grain boundary features.

When electron micrographs of the "slow" and "fast" etching regions were examined, no dramatic differences were evident, although the relief effects produced on etching the "L" zone are more noticeable than those in the "H" zone. These effects are undoubtedly due to the greater amount of precipitation in the "L" region.

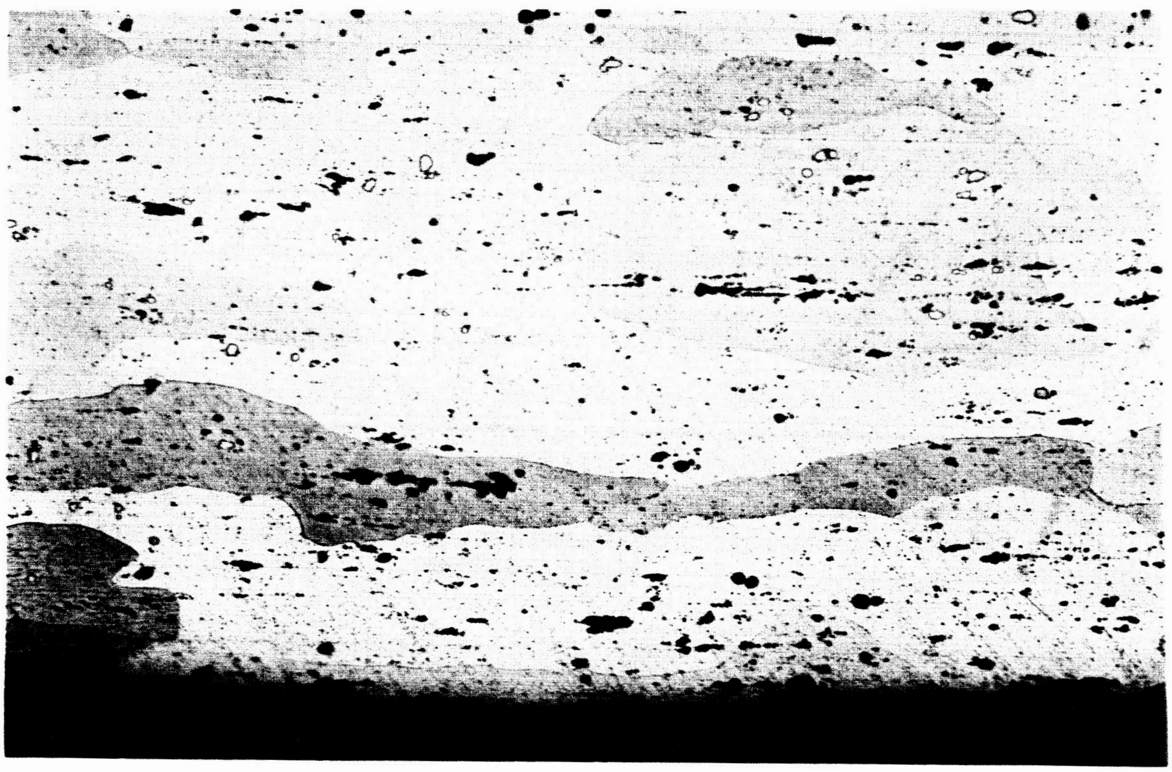
## F. Aging Studies

In the investigation of Type 2014 aluminum alloy (described later in this report) the effect of aging treatment on the milling qualities of the metal was found to be very great. Accordingly, it was decided to study various aging treatments for Type 2219 aluminum in the hope that more uniform chemical milling could be achieved in plates that had not received uniform quenching.

Accordingly, the experimental plan presented in Figure 11 was devised. The "normal" condition for 2219 is a room-temperature water quench followed by cold working. However, the cold work has little effect on milling rate, as shown earlier. The other quench conditions shown in Figure 11 were included to simulate the metallurgical conditions of the several areas

Neg. No. 29458 X250

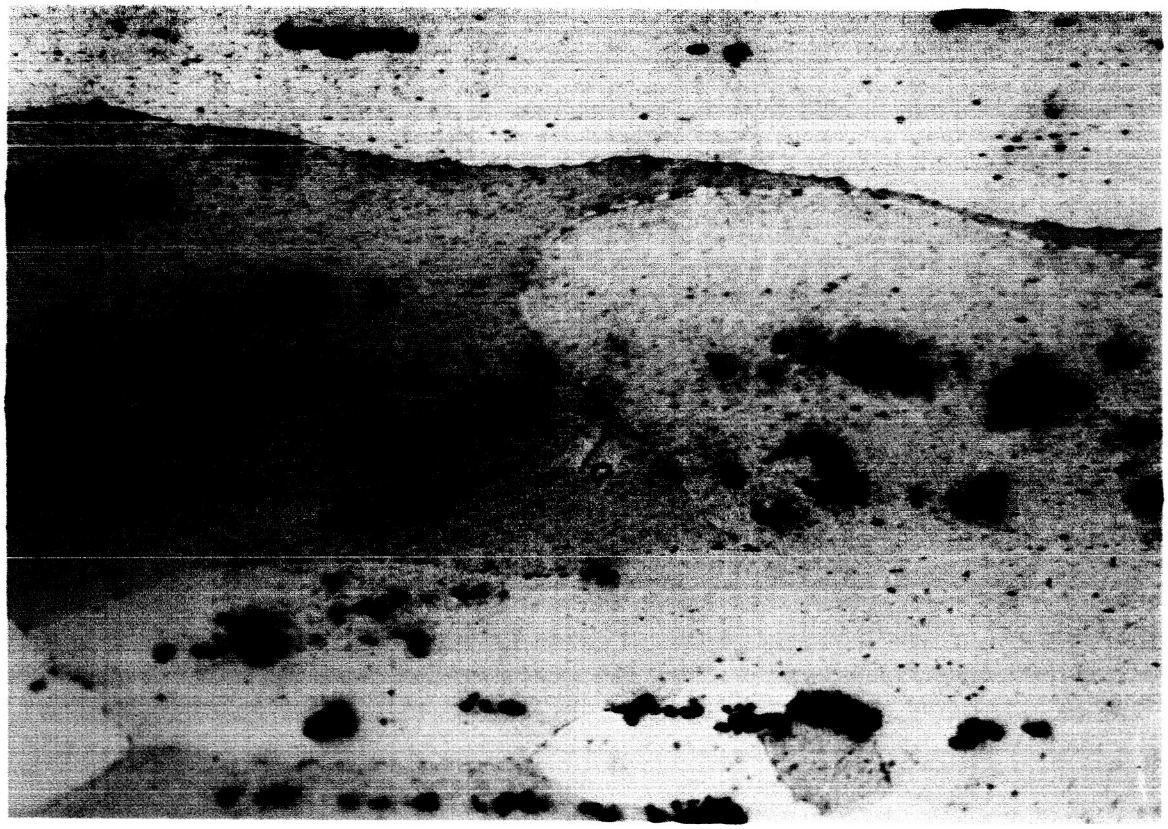
"Fast"-Etching Area. Note Grain Boundary Attack



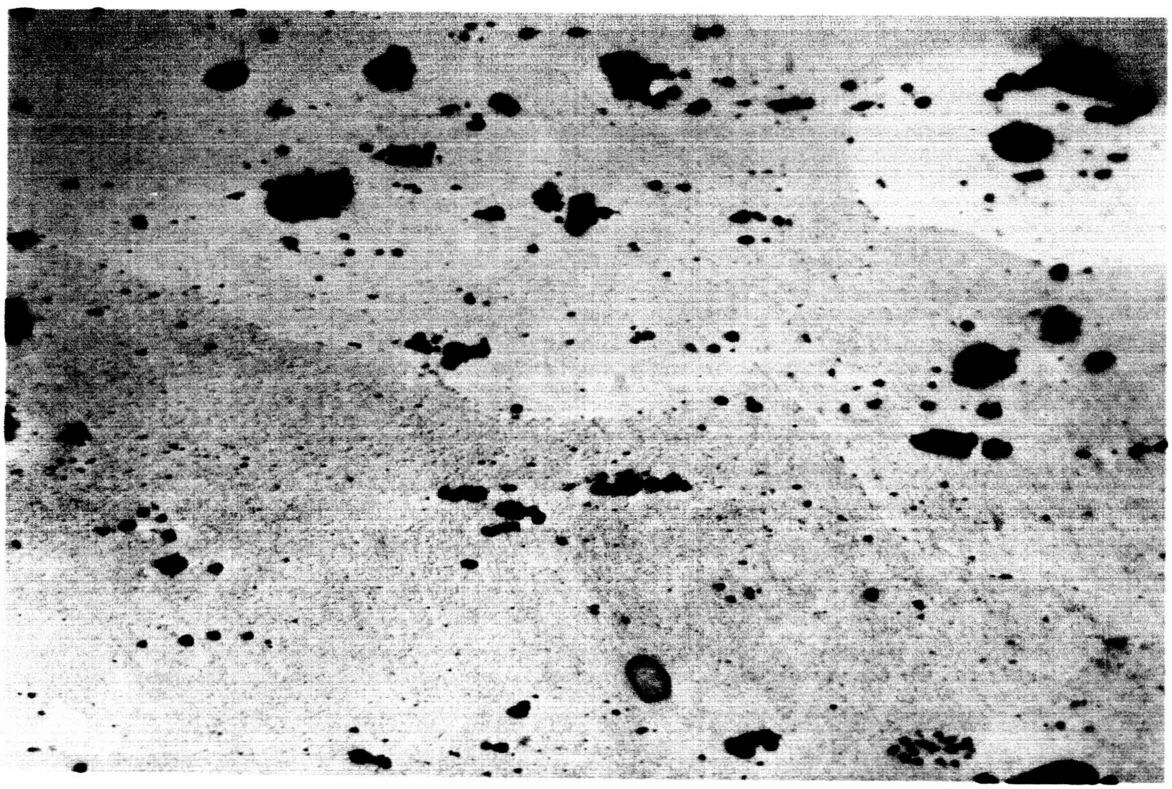
Neg. No. 29459 X250

"Slow"-Etching Area. Note Lesser Grain Boundary Attack

Fig. 9 - Structure of Type 2219-T37 Aluminum.

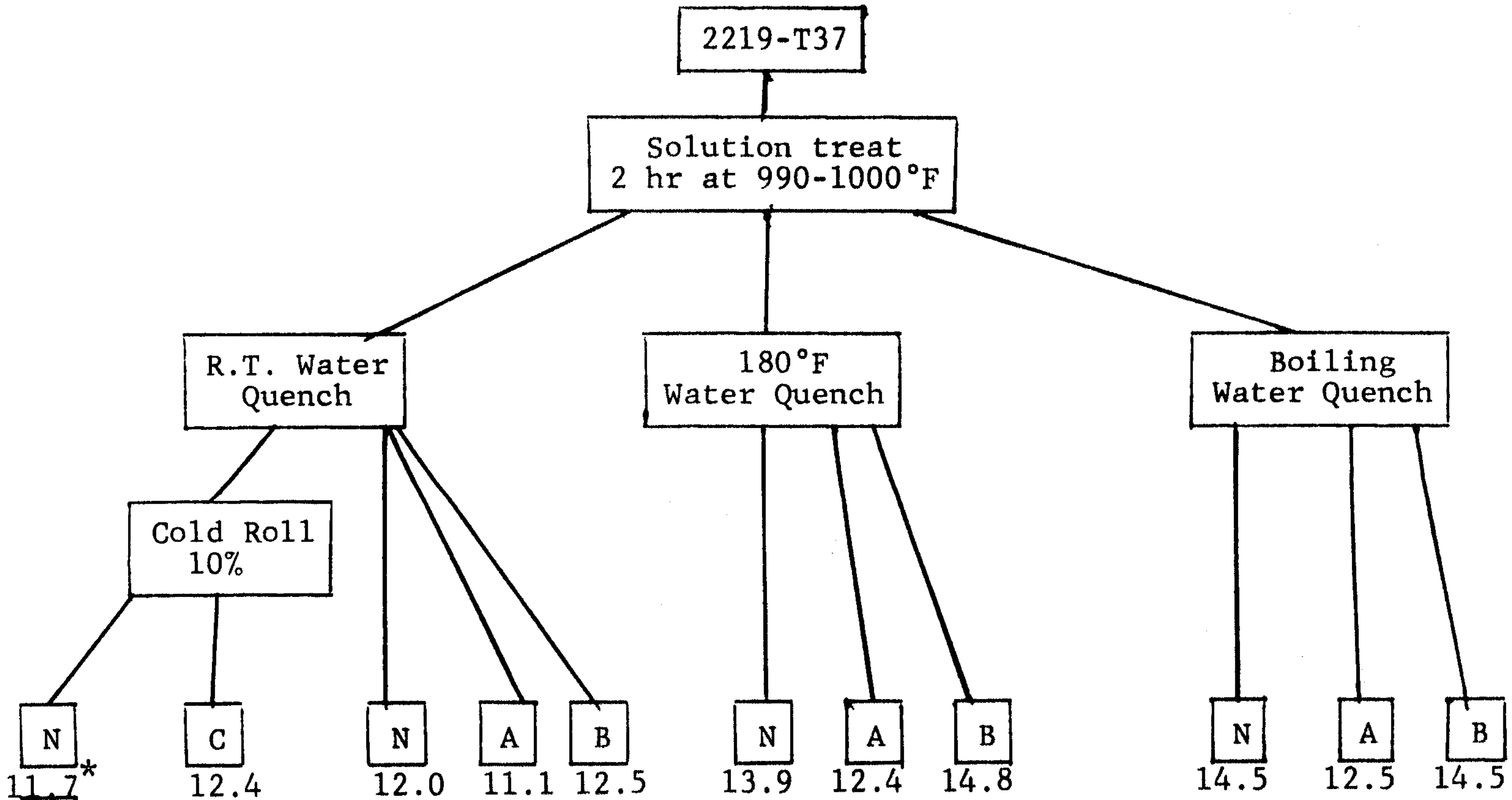


Neg. No. 29461 X1000
"Fast"-Etching Area. Note Precipitate-Free Grain Boundary Zones.



Neg. No. 29460 X1000
"Slow"-Etching Area. Note Lesser General Precipitation.

Fig. 10 - Structure of Type 2219-T37 Aluminum (same specimens as Figure 9, but higher magnification).




N — No further treatment

A — Standard artificial aging; 18 hr at 375°F

B — Overaged; 18 hr at 400°F

C — 10 hr at 350°F

* % Weight loss when chem-milled 15 min in NaOH (15 oz/gal, 190°F)

Fig. 11 - Study of Effect of Aging Treatment on Nonuniform Milling of Type 2219 Aluminum.

of a nonuniformly quenched plate. The aging treatments were included as possible methods for "erasing" the undesirable quench effects.

Duplicate specimens of each type were chemically milled for 15 min in NaOH (15 oz/gal, 190°F) and the weight losses measured. The results are shown, as average per cent weight loss, under each specimen type in Figure 11.

Comparison of the "no further treatment" specimens from the several quench temperatures shows the customary slower etch rate for room temperature quenched metal. Unfortunately, just about the same range of etch rates were shown by samples receiving aging treatments "A" and "B", so that one must conclude that the aging steps are not capable of correcting the metallurgical inhomogeneities responsible for nonuniform metal removal. It was noted, however, that the specimens quenched at 180°F and given the "standard" aging treatment ("A" in Figure 11) showed somewhat smoother milling than did the others. This is in accord with the results obtained on Type 2014 (discussed in a subsequent section).

## G. Conclusions

The composition of Type 2219 aluminum is such that its microstructure is quite sensitive to the thermal treatment received during manufacture. Because it has a very high level of alloying elements (especially copper, which is over 6%), all of the alloying ingredients cannot be taken into solution at the temperature of the "solution-treatment" (990°-1000°F). This means that the changes that occur during quenching of the alloy will be quite sensitive to cooling rate--more so than if all the alloying elements were in true solid solution at the elevated temperature. In the latter case, one might expect that formation of precipitates would be contingent on formation of centers of nucleation after quenching to the lower temperature and, hence, be relatively insensitive to the exact path of the temperature vs. time curve. But with undissolved precipitate already present throughout the alloy, the response to cooling would be immediate and a sensitivity to cooling rate would, therefore, be expected.

It should be emphasized that the mechanical properties of Type 2219 aluminum are not nearly so sensitive to the thermal treatment received during quenching as are the milling properties. A plate such as shown in Figures 8, 9, and 10 will undoubtedly satisfy specifications with regard to strength, ductility, and similar criteria. The differences in structure that are responsible for chemical milling variations are quite insignificant from the usual metallurgical point of view.

If alloys such as Type 2219-T37 must be chem-milled, then it appears essential that one of two approaches be followed: (1) incorporate quenching techniques that will avoid steam blankets on the plate, with consequent cooling irregularities; or (2) discover a chemical milling composition that will mask the electrochemical differences between fast and slow-quenched areas. This latter approach has been attempted, but with limited success. Certainly a promising direction would be the use of copper-complexing chemicals that are compatible with NaOH at high temperatures. The most obvious is cyanide, and it was, in fact, at least partly successful when tested sometime ago (Contract No. NAS 8-11718, Straza Industries, September 4, 1964). Attempts to discover other additives that would be nontoxic and more readily disposable were not promising (Contract No. NAS 8-11444, IIT Research Institute, April 29, 1965).

In summary, the successful chem-milling of Type 2219-T37 aluminum can probably best be achieved through modification of the quenching techniques employed by the alloy manufacturer. Vertical immersion quenching in water would very probably be superior to the spray-quenching currently used. The cost and inconvenience of these modifications, however, make it quite impractical. Since the discovery of chemical agents that avoid nonuniform milling in spite of metallurgical differences in the alloy also seems remote, it appears that a mechanical method of milling is a far more satisfactory solution. As pointed out earlier, this is the trend at present.

## IV. STUDIES OF TYPE 5456 ALUMINUM

### A. Yield Point Phenomena

This aluminum alloy contains about 5% magnesium and is readily weldable. Although not as high-strength as the copper and copper-zinc aluminum alloys, its weldability makes it desirable in certain applications.

One of the interesting features of this alloy is its tendency to form stretch marks when it is plastically deformed. These marks are, in fact, regions of nonuniform yielding, and result in the formation of localized bands of alternating thick and thin regions. Such bands can form in two distinct regions on the stress-strain curve of an alloy; one at the yield point, the other at a point near the ultimate strength of the metal.

These phenomena can best be illustrated by reference to Figure 12, in which a typical stress-strain curve for a specimen of annealed Type 5456 aluminum is plotted. This is a reproduction of the upper part of the curve, which was made on an Instron tensile testing machine.

There was no indication of visible bands formed at the yield point--there were essentially no true "Luder" lines, such as are often observed at the yield point of other metals. The nonuniform yielding at the top of the curve, however, was accompanied by the appearance of very pronounced and regularly spaced stretch marks. These latter marks were the subject of the present study.

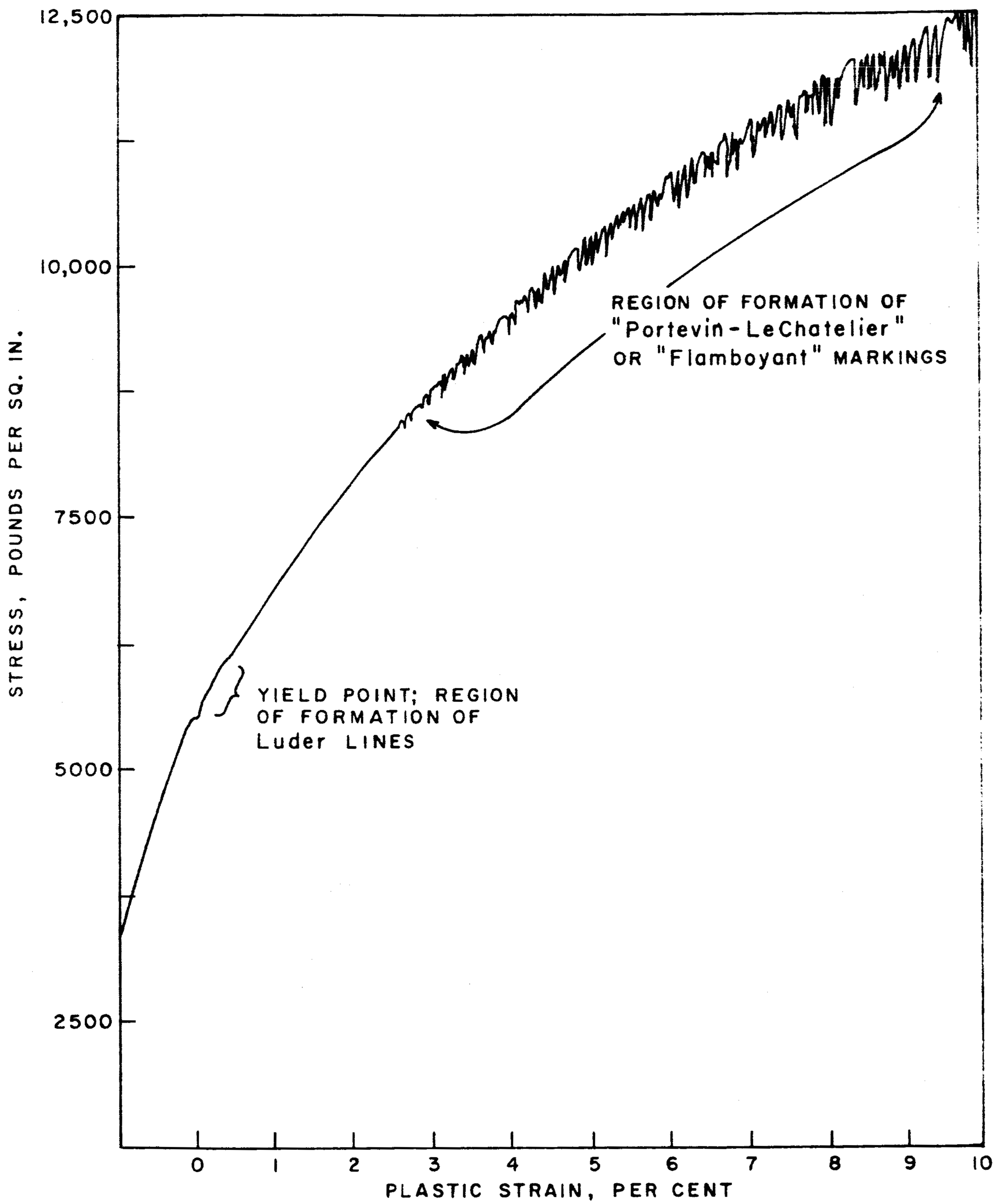



Fig. 12 - Upper Portion of Stress-Strain Curve for Type 5456 Aluminum Alloy.
(Solution Treated 2 hr at 850°F, furnace cooled.)

The question to be answered was whether or not the stretch marks just described can in any way influence the chemical milling characteristics of the 5456 alloy. Specifically, do they mill uniformly, do they become exaggerated, or do they tend to disappear during milling?

## B. Chem-Milling of Stretched Specimens

An experimental plan had been worked out earlier to answer these questions and at the same time to clarify the conditions under which the stretch marks appear. As shown in Figure 13, specimens of Type 5456-TO alloy were given various cold-rolling treatments from 0 to 30%, after which they were stretched as indicated. The object was to determine how preliminary cold work by rolling might be employed to prevent formation of Luder lines. However, as pointed out already, this alloy does not form true Luder lines, and the problem was resolved into a study of the "flamboyant markings" which appear at very high total strains. Nevertheless, the information obtained was quite valuable because it showed that the stretch marks are much more pronounced when an annealed specimen is stretched than when a cold-rolled specimen is stretched.

In Figure 13 the specimens that showed stretch marks visible to the eye are indicated by an asterisk above the appropriate box.

These 24 specimens were scanned with a "proficorder" and records made of the surface contour of each specimen prior to chem-milling. They were then milled to a depth of about 0.0025 in. on each side, and the profile again recorded. This sequence was then repeated after milling an additional 0.006 in. from each side.

The data are entirely too voluminous to permit presentation of all of the profiles. It will suffice to illustrate the effects found with selected series of traces.

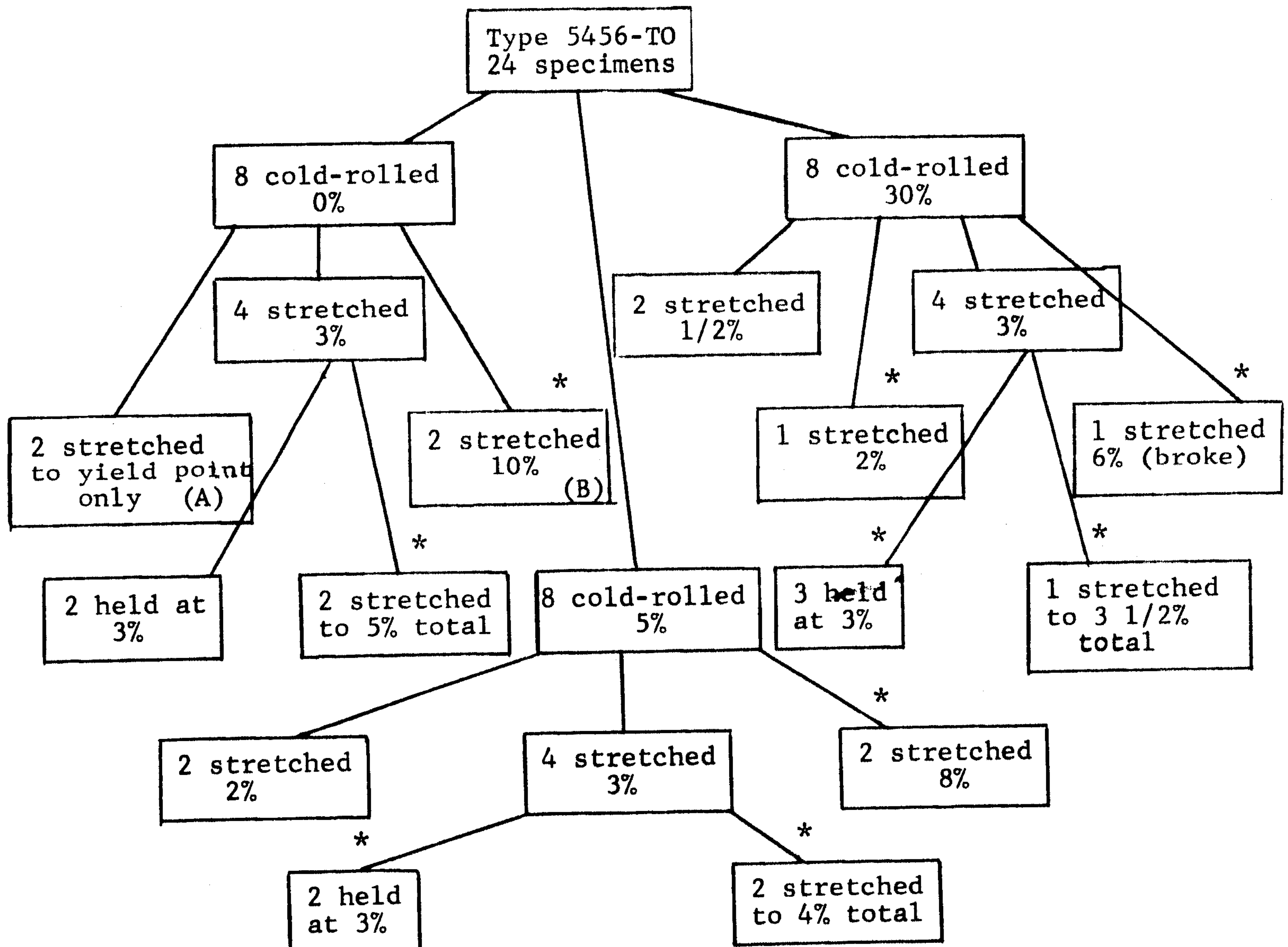



Fig. 13 - Preparation of Specimens of Type 5456 Aluminum for Stretch-Mark Study. Specimens from group "A" shown in Fig. 14; Specimens from group "B" shown in Fig. 15.

In Figure 14 are shown the traces before milling and after two successive milling steps, for a specimen that showed no stretch marks prior to chem-milling (taken from group "A" of Figure 13). Shown in Figure 15 are the results of milling a specimen which was subject to pronounced stretch marking (from group "B" of Figure 13). The results are clear--the stretch marks are neither accentuated nor erased by chemical milling in NaOH.

To clarify the matter of exactly when the stretch marks appear in the practical fabrication of space vehicles, a further series of specimens were stretched, scanned, chem-milled, and scanned again. At the same time, certain of these specimens were chem-milled in other etching media to determine whether the marks could be removed by those media.

It was found that stretch marks appear in the Type 5456-H343 material after it is stretched about 4 1/2%. Thus, if this type of material must be stretched to this degree during fabrication, marks must be expected, even though they were absent in the alloy as received from the mill. Furthermore, the stretch marks cannot be removed during milling. These points are illustrated in Figures 16, 17, 18, and 19, which are self-explanatory.

## C. Conclusions

Strain markings are produced in Type 5456 aluminum regardless of its past thermal or mechanical history. Once produced, these markings are neither removed nor made more pronounced by chem-milling. Results of limited experiments in proprietary etchants make it quite unlikely that any different results will be obtained in other milling media. That is, the evidence is that stretch marks are not electrochemically significant in the chem-milling process. Rather, they are simply mechanical effects that produce dimensional variations in the metal, but do not cause any acceleration or deceleration of milling.

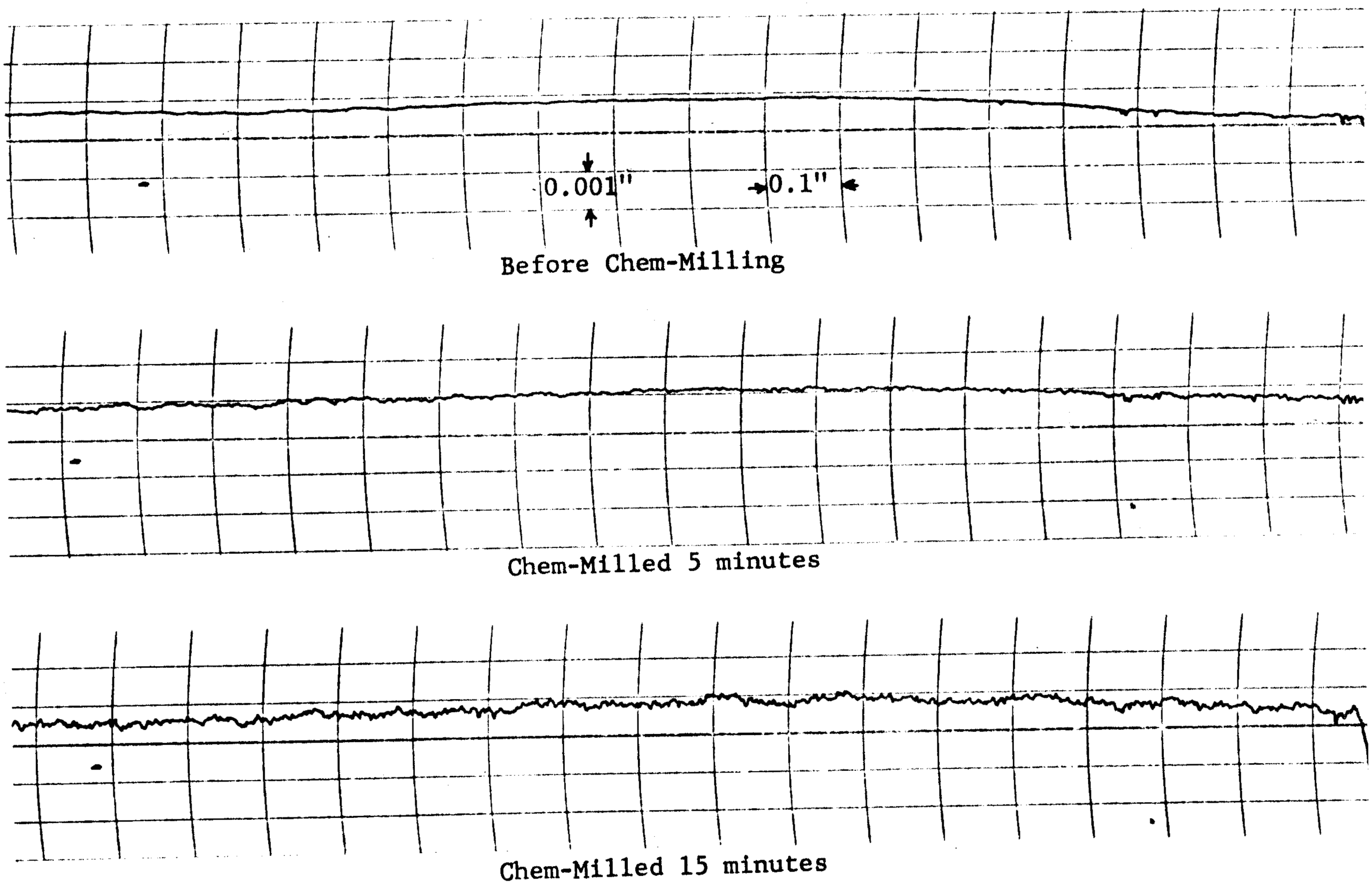
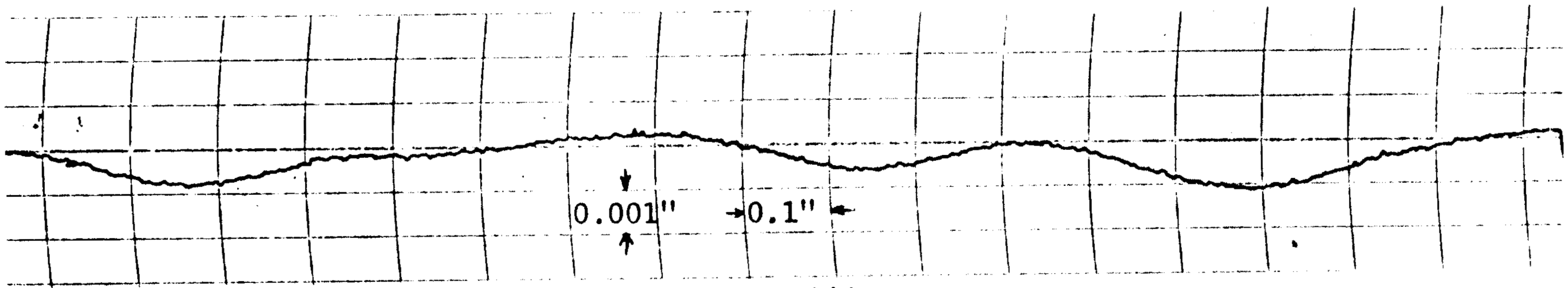
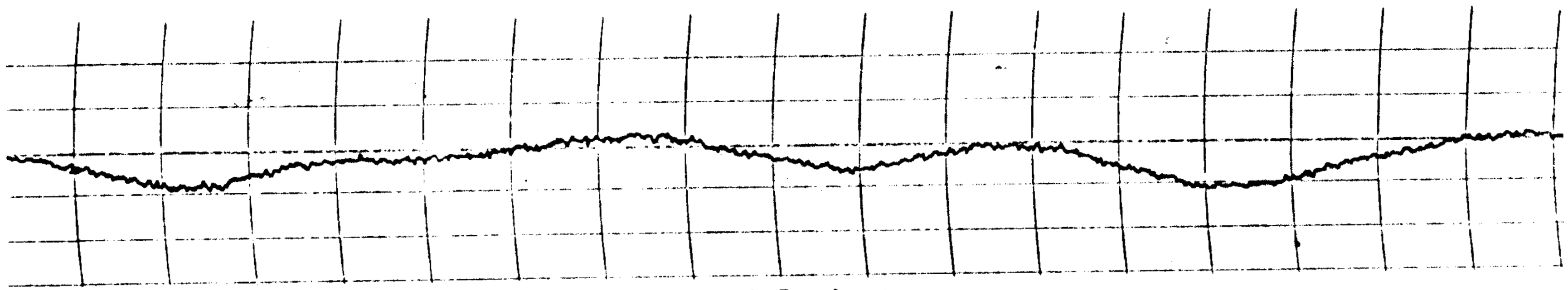


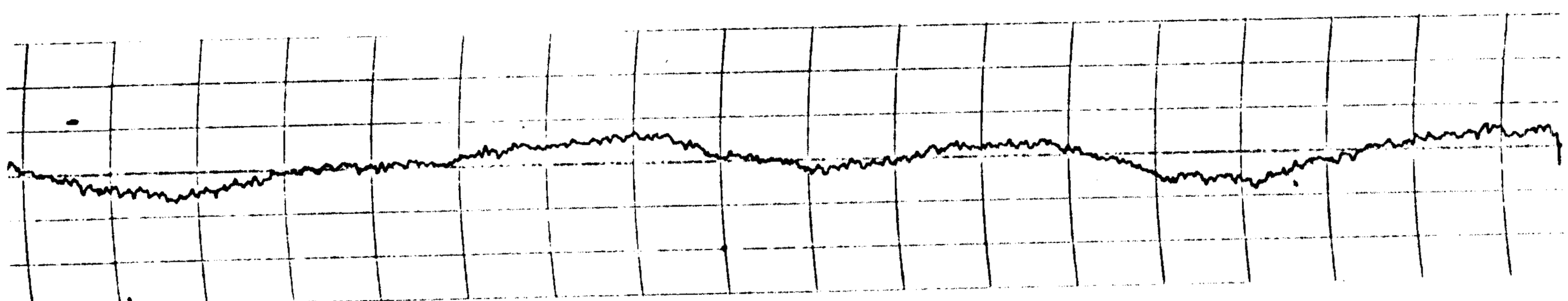

Fig. 14 - Proficorder Traces of Type 5456 Aluminum with No Stretch Marks. Chem-Milled in NaOH, 15 oz/gal, 170°F. (Specimen from group "A" of Fig. 13)




Before Chem-Milling



Chem-Milled 5 minutes



Chem-Milled 15 minutes

Fig. 15 - Proficorder Traces of Type 5456 Aluminum with Pronounced Stretch Marks. Chem-Milled in NaOH, 15 oz/gal, 170°F. (Specimen from group "B" of Fig. 13)

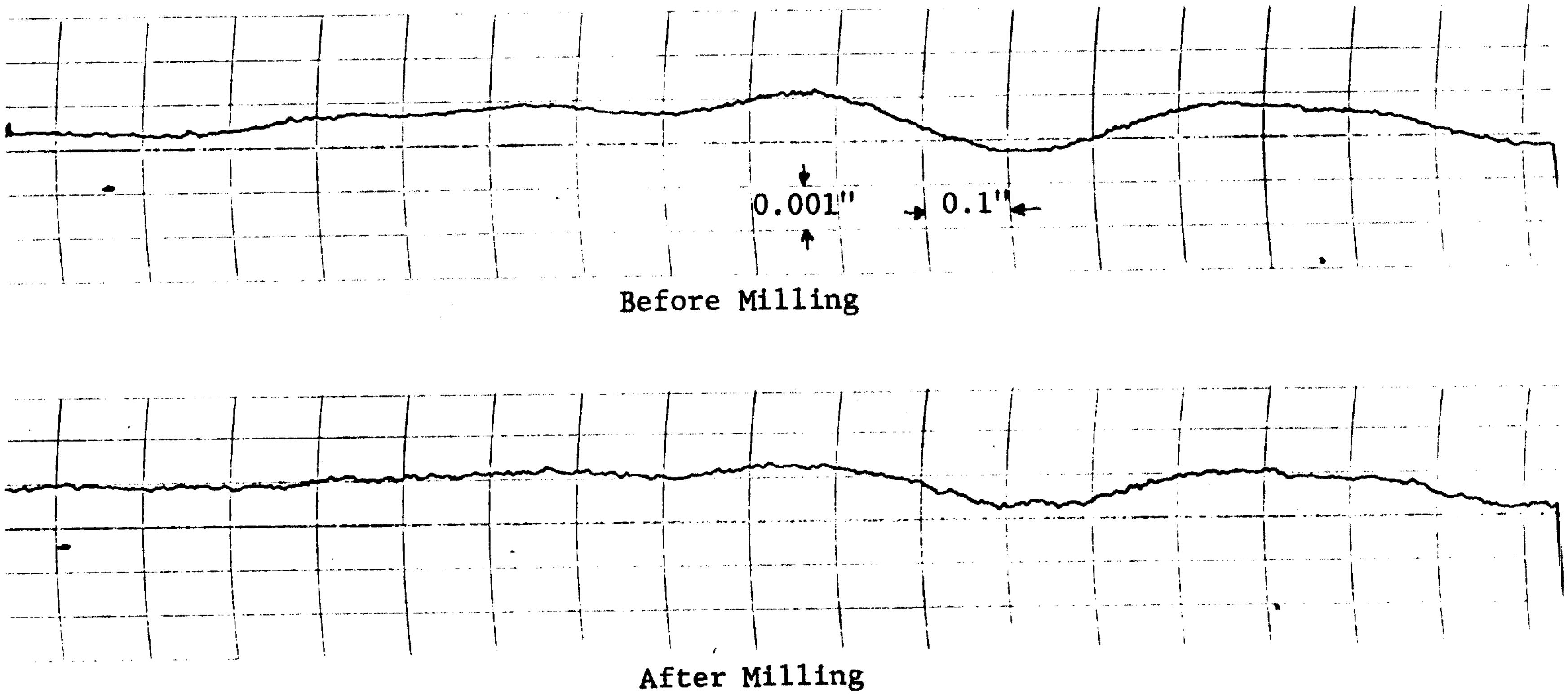



Fig. 16 - Chem-Milling of Stretch-Marked Type 5456-H343 Aluminum in NaOH.

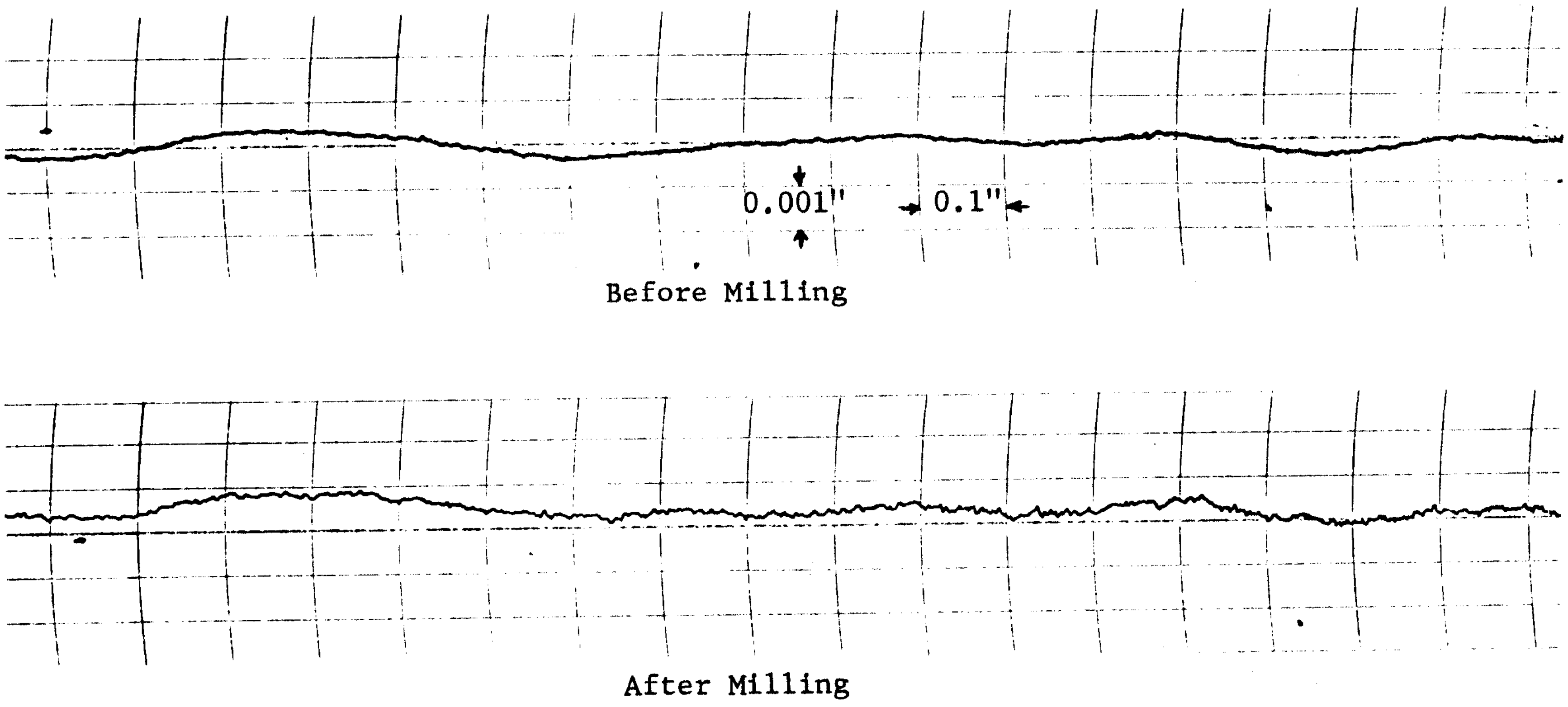



Fig. 17 - Chem-Milling of Stretch-Marked Type 5456-H343 Aluminum in Turco Etchant.

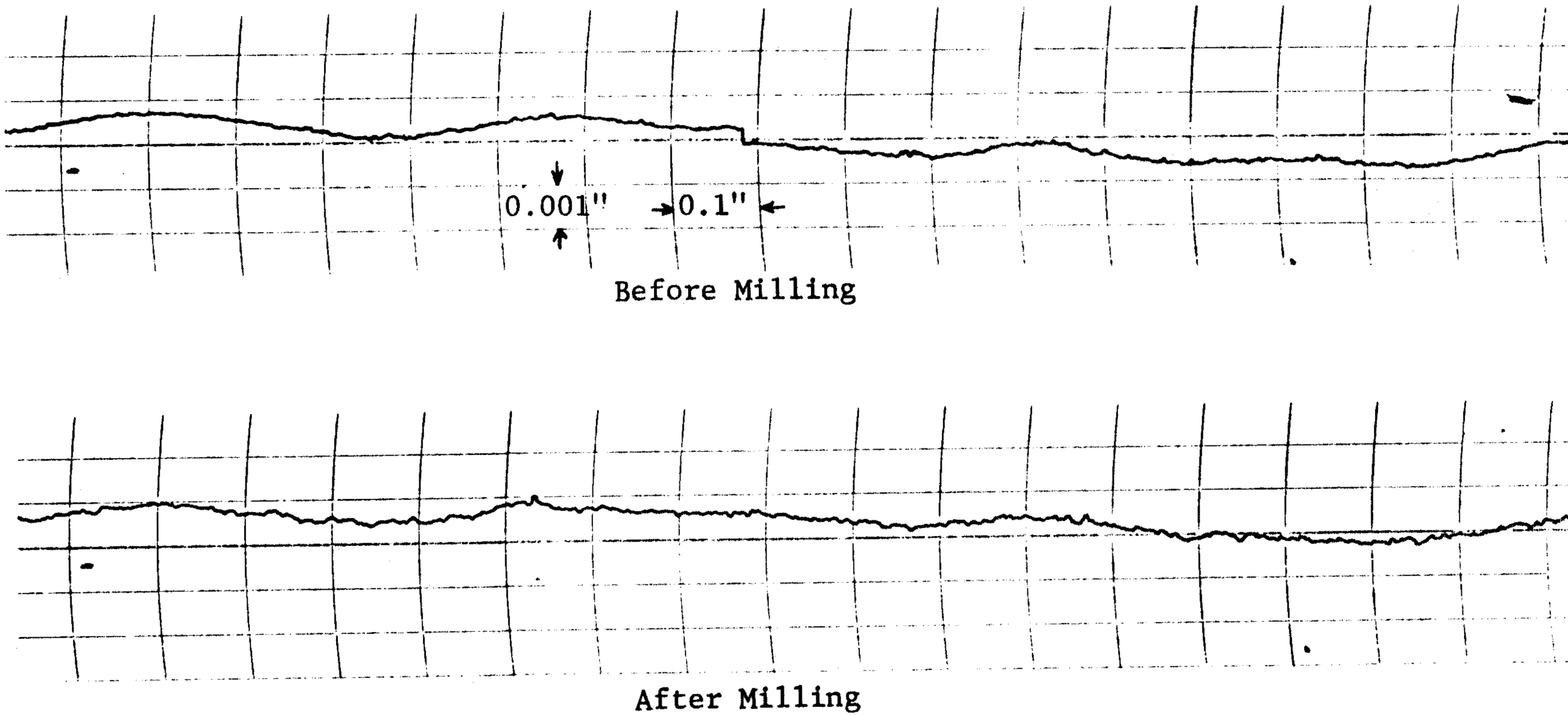



Fig. 18 - Chem-Milling of Stretch-Marked Type 5456-H343 Aluminum in Wyandotte Mil-Etch.

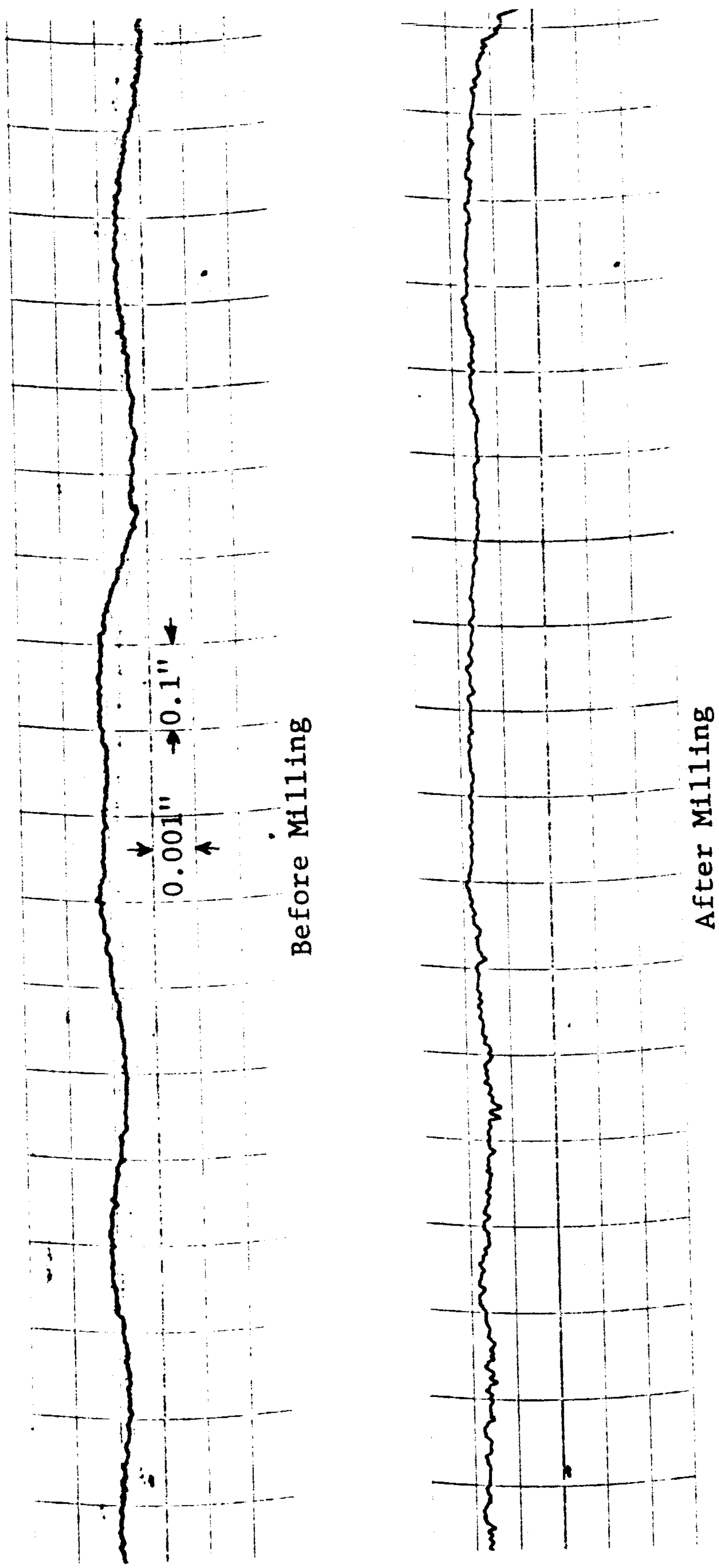



Fig. 19 - Chem-Milling of Stretch-Marked Type 5456-H343 Aluminum in Ferric Chloride.

If the dimensional effects of stretch marks must be avoided in space vehicles, the forming must be done at sufficiently low levels of deformation that the strain markings do not appear.

## V. STUDIES OF TYPE 2014 ALUMINUM

### A. Rough Etching

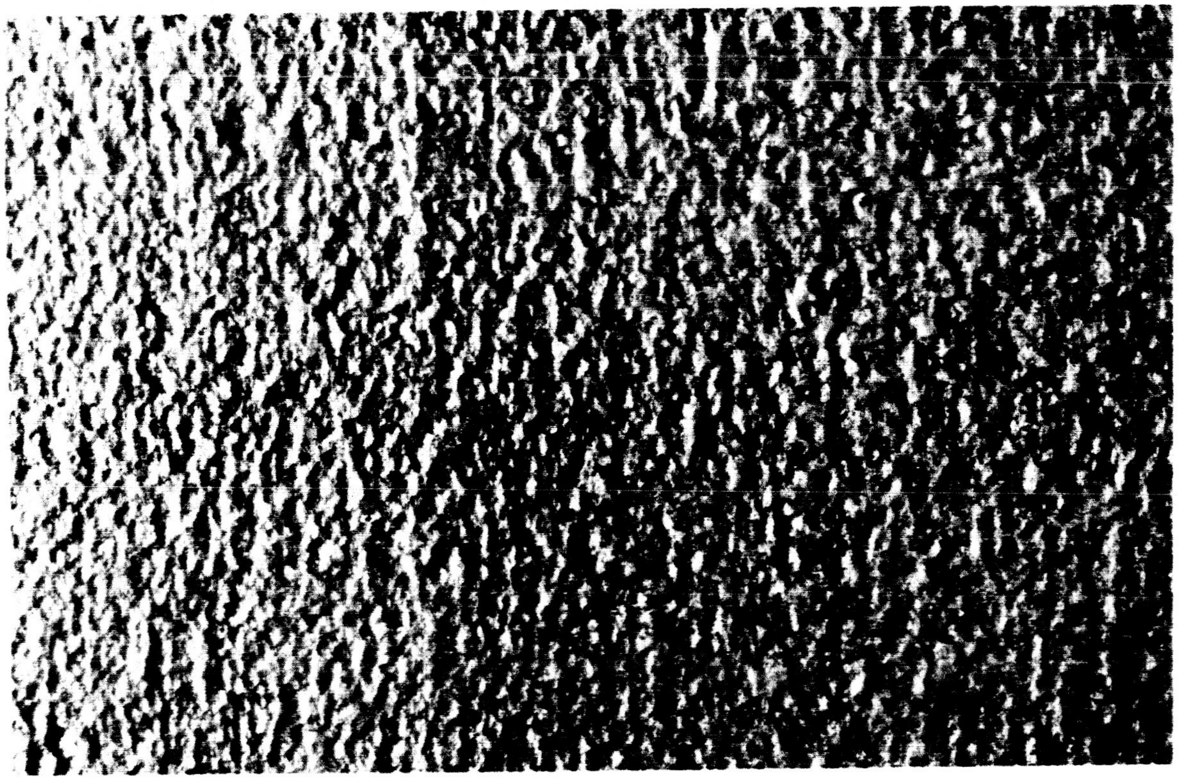
The chief difficulty met in the chem-milling of Type 2014 alloy is the tendency to develop a rough surface. Specifically, the 2014-T451 material (naturally aged after solution heat treatment) becomes rough on milling, whereas 2014-T651 mills quite well, retaining a satin smooth surface.

Typical surfaces of 2014-T451 and 2014-T651 after milling for 15 min in NaOH (15 oz/gal) at 170°F are shown in Figure 20. That such dissimilar behavior could result from the relatively minor microstructural differences between the T4 and T6 temper is rather surprising. Accordingly, a series of experiments were designed to study the effect of solution treatment temperature, aging routine, and alloy composition variations on the milling properties of Type 2014 alloy.

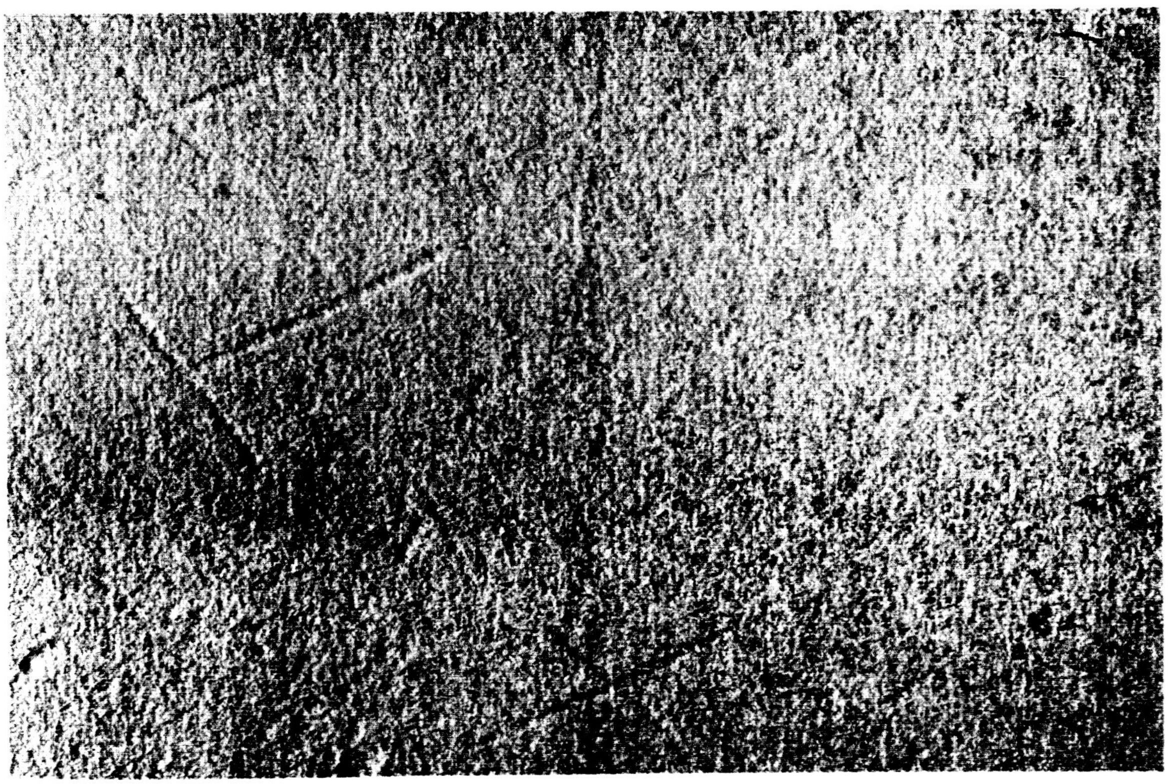
### B. Aging Variations

The experiment shown in Figure 21 was designed and carried out. The starting material was a sample of Type 2014-T651 plate, approximately 0.25 in. thick. Preliminary experiments showed that this plate gave a very smooth surface when chem-milled in NaOH, whereas a sample of 2014-T451 plate (from a different lot of material) showed relatively rough etching (Figure 20).

The plan (outlined in Figure 21), therefore, was to determine if the T651 material would yield a rough surface if converted back to a T4 condition by solution treatment and quenching, and if it would become smooth-milling once more when artificially aged.



Neg. No. 31241 Naturally Aged 10X



Neg. No. 31242 Artificially Aged 10X

Fig. 20 - Comparison of Milling Characteristics of Naturally Aged and Artificially Aged Type 2014 Aluminum.

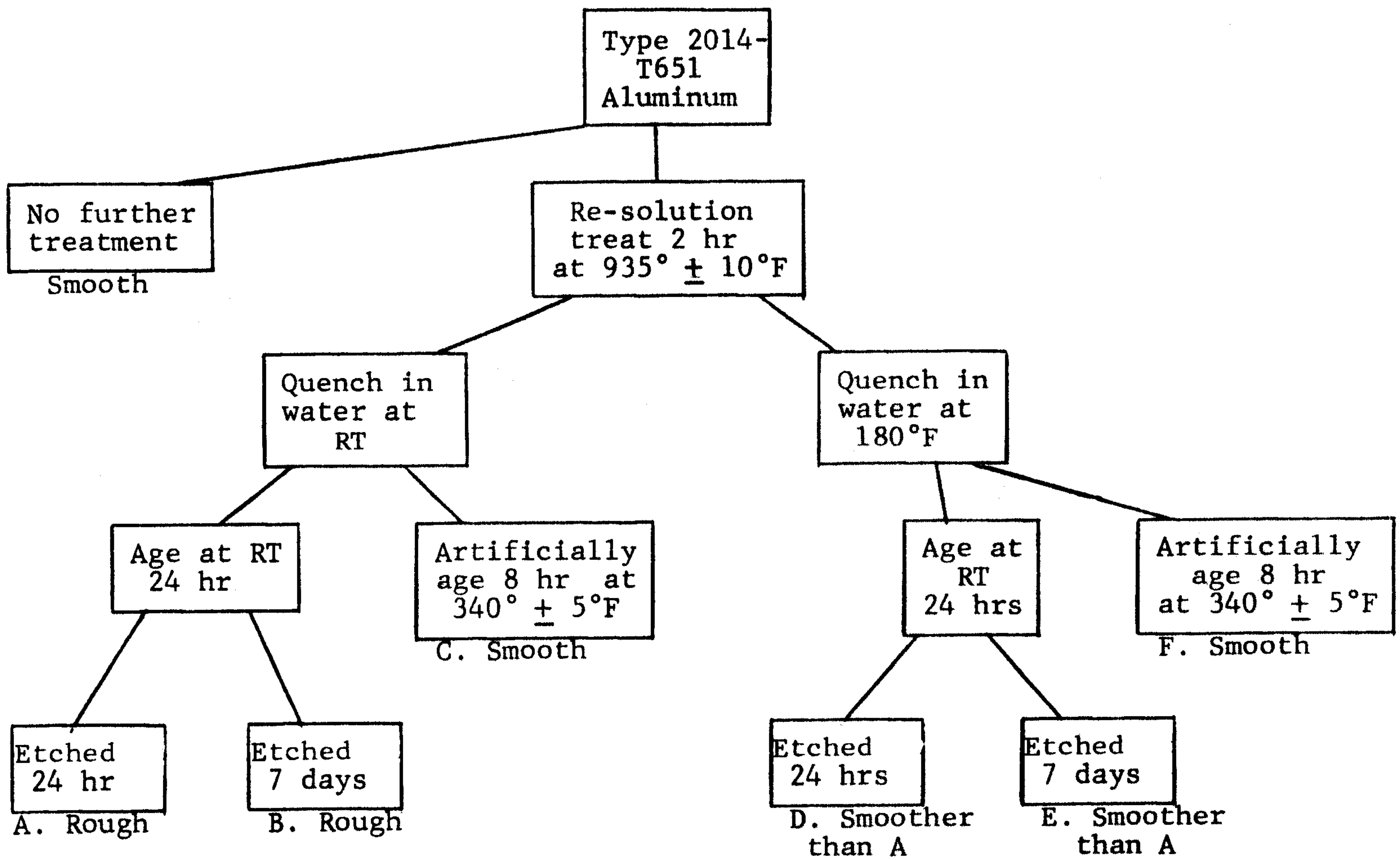



Fig. 21 - Effect of Aging on Milling of Type 2014 Aluminum

The milling results are given under each of the boxes in Figure 21. One very striking result was that this particular lot of 2014 alloy did not yield nearly so rough a surface when milled in the naturally aged condition as did the other lot of Type 2014 (originally received in the T451 condition). The difference between the naturally-aged and artificially-aged states was apparent, however, even in the less "age-sensitive" alloy.

It should be noted here that the quenching temperature did not seem to influence the milling characteristics of the alloy, nor did the length of time of aging at room temperature affect the milling smoothness.

Obviously, the next experiment was to repeat the aging comparison with the other lot of Type 2014 alloy. This was carried out as shown in Figure 22, in which the quench temperature was not varied. The milling results are shown in Figure 22, under each etching condition.

It will be noted that this lot of metal showed a very strong reaction to the aging treatment, even though chemical analysis showed both lots of 2014 alloy to be nominally the same material. One can only conclude, therefore, that minor chemical differences in the alloy do indeed influence its response to aging treatments and, in turn, its milling characteristics. In order to clarify this point, however, it would be necessary to study dozens of specimens from different lots of 2014, and to correlate the aging behavior (and milling qualities) with the chemical analysis.

One further experiment was performed, however, with the object of determining the minimum temperature at which artificial aging would make itself evident in the milling properties of the alloy. The aging time was selected arbitrarily at 5 hr, and a series of samples of solution-treated and quenched Type 2014 aluminum were treated at temperatures from 260° to 340°F.

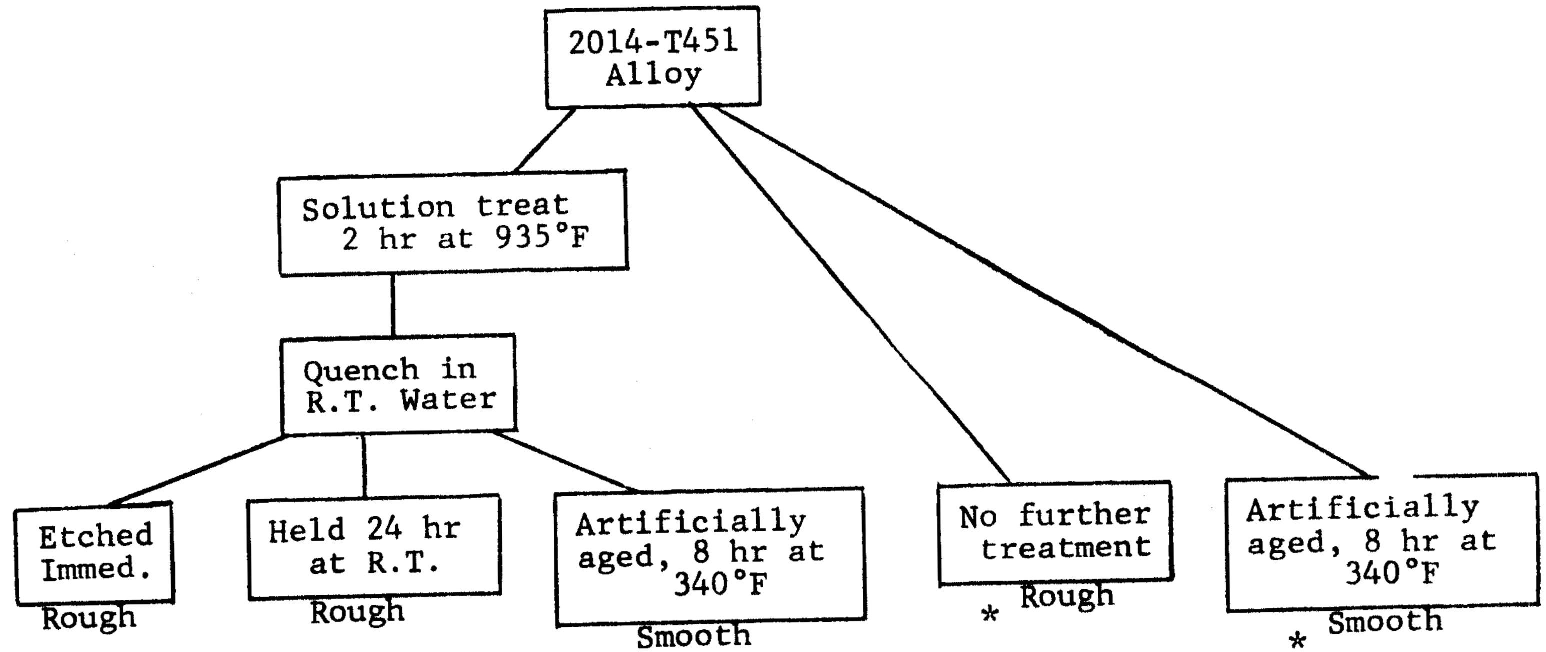



Fig. 22 - Comparison of T4 and T6 Conditions on Milling of Type 2014 Aluminum.
*Specimens examined with electron microprobe (Fig. 24)

The results of milling tests on these specimens are shown in Table II. Clearly, the onset of smooth milling occurs at a temperature close to 320°F.

## C. Solution Treatment Temperature

It was at first considered possible that the remarkable difference in the two alloy lots discussed above might be due to a difference in the solution treatment each had received during manufacture. Accordingly, a number of specimens of Type 2014-T651 were given the several treatments summarized in Figure 23. Three different solution treatments were compared, the specimens being quenched in water at room temperature. For the "standard" solution treatment temperature of 935°F, samples were quenched and stored in different ways before milling to check the influence of aging temperature.

The results are given below each box in Figure 23. It is clear that neither the exact solution-treatment temperature nor the aging temperature had significant effects on the milling qualities of the alloy. While not as rough as samples from Figure 22, all the specimens of Figure 23 were essentially "rough-milling" as compared to artificially aged specimens of the same lot of alloy.

## D. **Electron Microprobe Study of Aging**

In the hope that a significant difference might be found in the distribution of the principal alloying ingredient (copper) between the naturally and artifically aged conditions, microprobe specimens were taken from the samples marked with an asterisk in Figure 22.

The specimens were scanned at an X-ray wavelength selected to detect copper in the alloy. Both electron micrographs and copper distribution patterns are presented in Figure 24, for both naturally and artificially aged specimens taken from the same lot of alloy.

TABLE II

EFFECT OF AGING TEMPERATURE ON MILLING ROUGHNESS IN TYPE 2014 ALLOY

| Aging Temperature, °F | Specimen Weight Loss, % | Surface Condition |
|---|---|---|
| 75 | 15.8 and 18.6 | Rough |
| | 18.3 | Rough |
| 200 | 15.9 | Rough |
| | 16.2 | Rough |
| 280 | 14.3 | Rough |
| | 14.5 | Rough |
| 300 | 14.9 | Rough |
| | 14.5 | Rough |
| 320 | 16.4 | Smooth |
| | 16.2 | Smooth |
| 340 | 16.5 | Smooth |
| | 15.9 | Smooth |
| | 15.0 | Smooth |

All specimens solution-treated at 935°F for 2 hr, quenched in water at room temperature, aged for 5 hr at various temperatures. Chem-milled in NaOH (15 oz/gal) for 15 min.

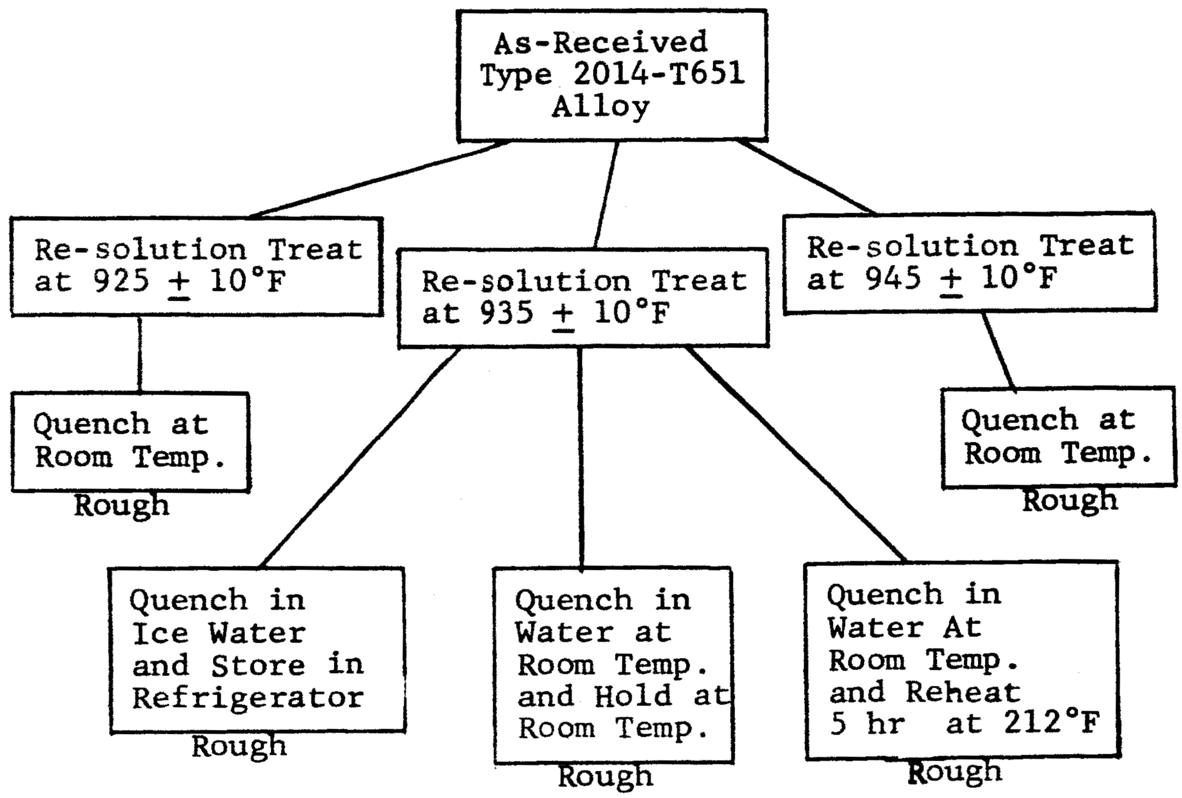
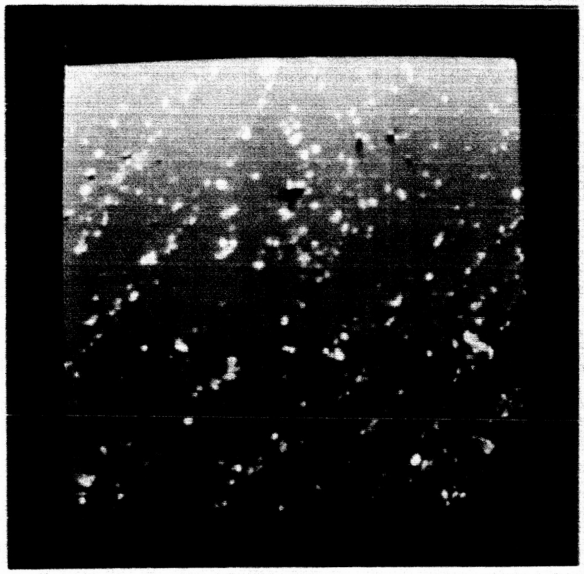
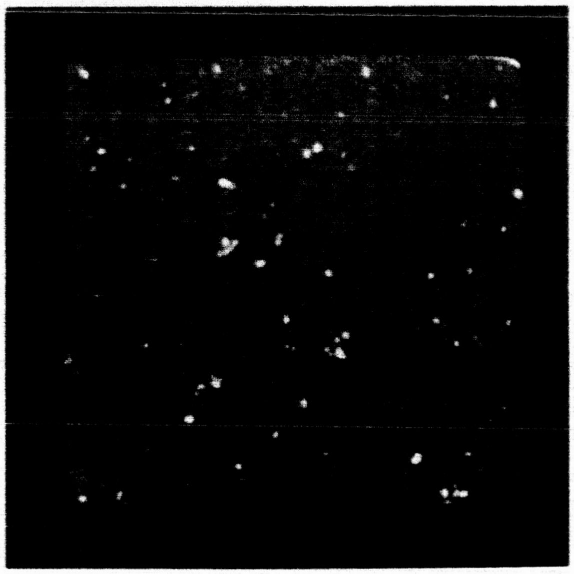


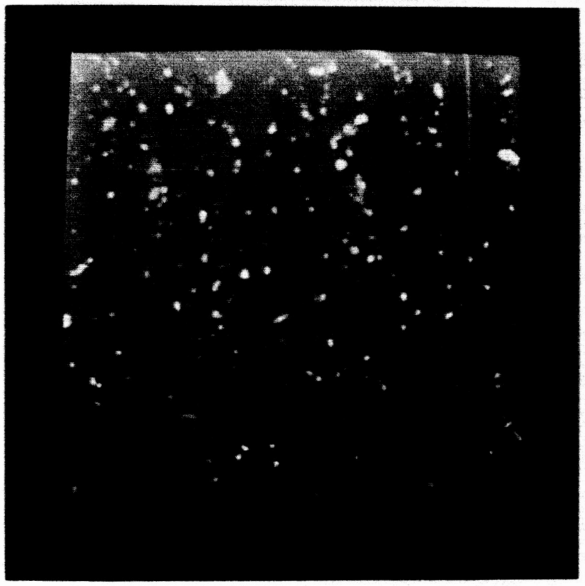

Fig. 23 - Study of Solution Treatment Temperature on Milling of Type 2014 Aluminum.

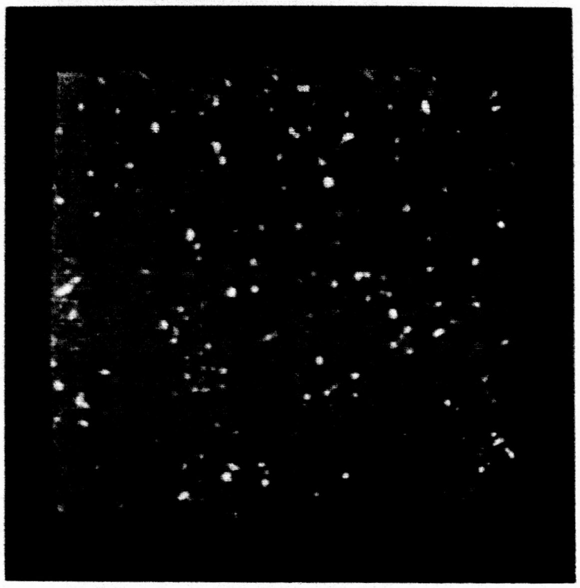




Electron Image X170 Cu Radiation Image X170

Naturally Aged





Electron Image X170 Cu Radiation Image X170

Artificially Aged

Fig. 24 - Electron Microprobe Pictures of Type 2014 Aluminum.
(Specimen preparation shown in Fig. 22)

The pictures indicate that there is no structural difference of consequence in the two samples--a result not unexpected in view of the very slight movement of elements that will accompany a heat treatment of so mild a nature as artificial aging at 340°F.

## E. Milling In Other Reagents

A comparison of the milling characteristic of Types 2014-T451 and 2014-T651 in several additional solutions was carried out. Surprisingly, the rates of attack were quite different for the two tempers when they were milled in ferric chloride. They were much more nearly the same in all the alkaline media, but the artificially aged material consistently underwent more rapid attack. The data are shown in Table III.

## F. Time and Temperature Effects of Milling

It was considered desirable to learn whether the roughness developed in milling the T4 temper of 2014 alloy is a function of the metallurgical structure only, or if it is affected significantly by the temperature-time combination used. That is, does the roughness depend merely on removing a certain depth of metal, or does the amount of roughness vary with the rate of removal?

Accordingly, the experiment outlined in Figure 25 was designed and carried out. Three different temperatures were used and four times of milling, selected to produce comparable depths of removal on all specimens. The per cent weight loss is recorded for each specimen, together with the surface finish produced.

It is clear from these data that in this etching medium, the time and temperature of milling are of secondary importance in determining the surface finish produced. The roughness is developed in the T451 material at a weight loss of approximately 10-15% (corresponding to about 0.012-0.018 in.), whereas the T651 is smooth in all cases, regardless of depth of penetration.

## TABLE III

## MILLING RATES FOR TYPE 2014 ALUMINUM IN VAROUS MEDIA

| Aging Condition | Time, min | Specimen Weight Loss, % |
|---|---|---|
| | NaOH, 15 oz/gal, 170°F | |
| Natural | 5 | 5.3 |
| Natural | 15 | 15.8 |
| Artificial | 5 | 5.5 |
| Artificial | 15 | 16.5 |
| Natural | 5 | 6.1 |
| Natural | 15 | 18.3 |
| Artificial | 5 | 5.0 |
| Artificial | 15 | 15.9 |
| Natural | 5 | 6.2 |
| Natural | 15 | 18.6 |
| Artificial | 5 | 5.0 |
| Artificial | 15 | 15.0 |
| | $FeCl_3$, 42° Baumé , Room Temperature | |
| Natural | 5 | 1.0 |
| | 10 | 2.0 |
| | 15 | 31.4 |
| Artificial | 5 | 1.9 |
| | 10 | 38.8 |
| | 15 | 100 |
| | Turco, 190°F | |
| Natural | 15 | 12.4 |
| Artificial | 15 | 13.9 |
| | Mil-Etch, 190°F | |
| Natural | 15 | 16.2 |
| Artificial | 15 | 23.2 |

Type 2014-T451

| | 5 min. | 10 min. | 15 min. | 20 min. |
|---|---|---|---|---|
| 190°F | Rough 16.4% | Rough 13.7% | | |
| 170°F | | Semi-Rough 9.3% | Rough 13.8% | |
| 160°F | | | Semi-Rough 3.3% | Rough 14.4% |

Type 2014-T651

| | 5 min. | 10 min. | 15 min. | 20 min. |
|---|---|---|---|---|
| 190°F | Smooth 15.5% | Smooth 15.1% | | |
| 170°F | | Smooth 9.6% | Smooth 14.4% | |
| 160°F | | | Smooth 6.0% | Smooth 15.2% |

Fig. 25 - Time and Temperature Effects on the Milling of Type 2014 Aluminum.

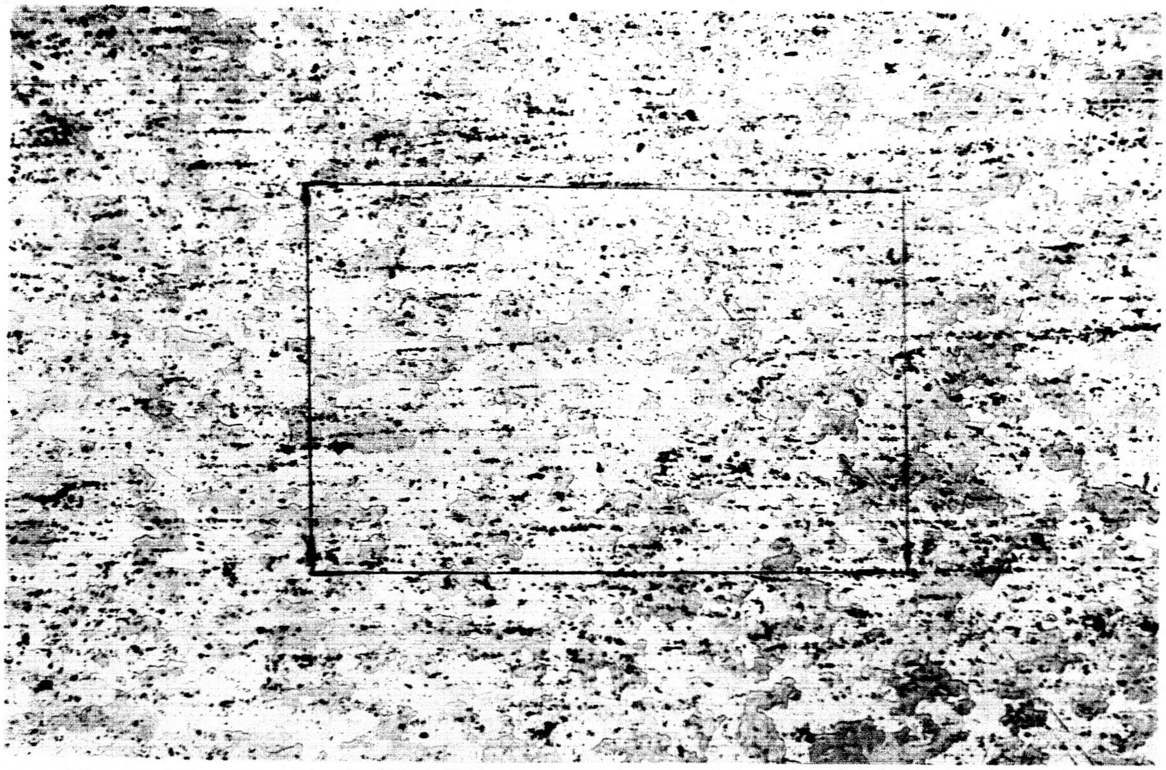
While this by no means implies that it is impossible to mill the T4 temper smoothly (see discussion later), it certainly is reasonable to conclude that it is not likely that it can be done with simple variations in the mode of operation of a sodium hydroxide solution.

## G. Microscopic Study of Roughness Development During Milling

In an effort to correlate the metallurgical structure of Type 2014 alloy with its milling behavior, a series of photographs were made of selected areas of 2014 specimens after different periods of milling. Although it was very difficult to identify a particular area of a specimen after more than about 1 min of milling in NaOH, the pictures that follow can be directly superimposed throughout the milling sequence (10-15 min).

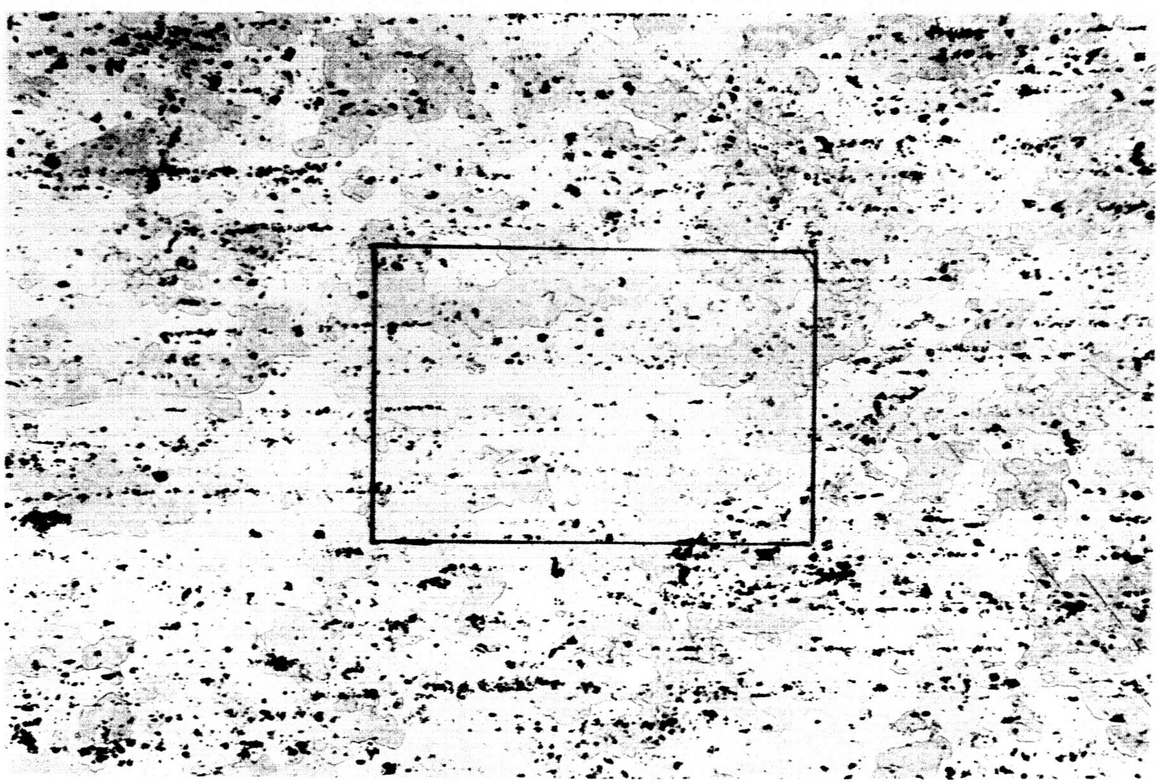
Samples of Type 2014-T451 and Type 2014-T651 were polished metallographically, etched to reveal structure, and photographed at different magnifications prior to milling, as shown in Figures 26 and 27. Holes were drilled in the specimens to serve as reference points in photographing the same area at various stages of chem-milling. The sequence of pictures for both tempers are shown in Figures 28 and 29, with the final appearance of the specimens shown in Figure 30.

Obviously, roughness develops very rapidly and obliterates the original structure. Nevertheless, it is quite clear that the "hills and valleys" that develop are of a much larger dimension than the microstructural features of the alloy. One must conclude, therefore, that roughness is "self perpetuating" in certain alloys that favor it, but that the roughness is not caused by "selective etching" of certain grains or certain microconstituents. More will be said of this later.



Neg. No. 30835

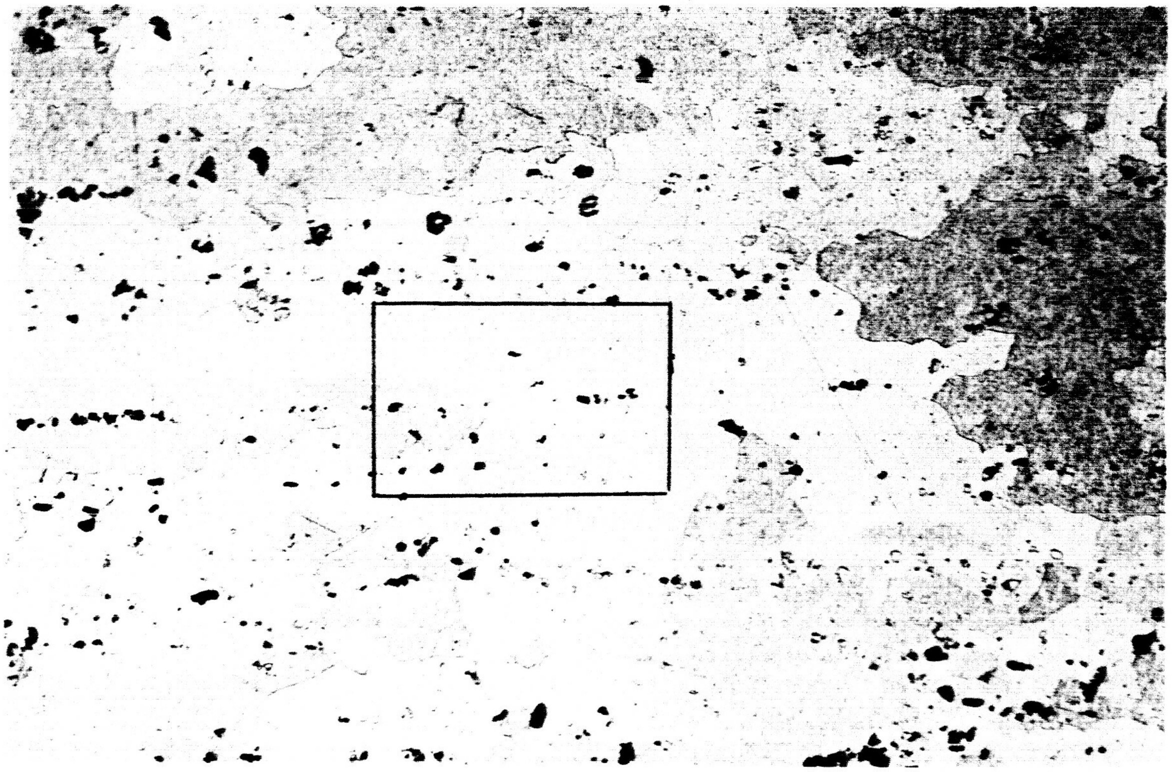
(a) Magnification 50X



Neg. No. 30836

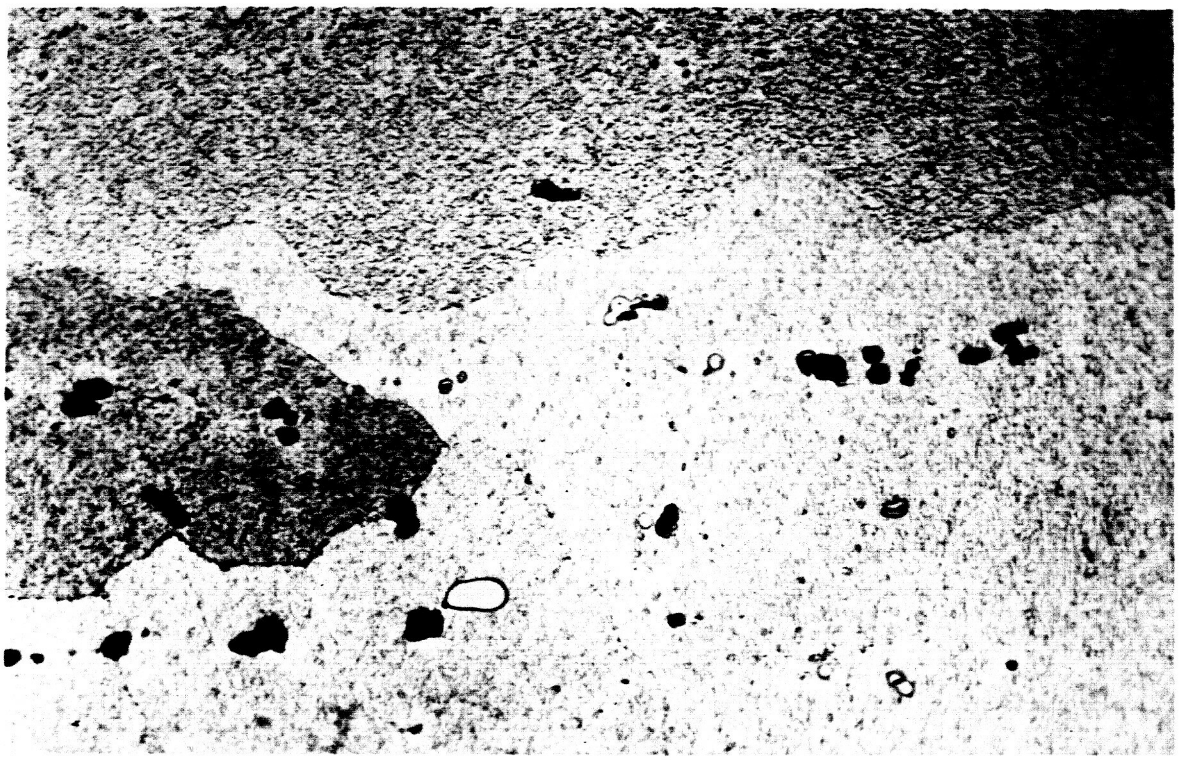
(b) Magnification 100X

Fig. 26 - Structure of Type 2014-T451 Aluminum Before Chem-Milling (Naturally Aged). Rectangles Show Area of Next Higher Magnification. Keller's Etch.



Neg. No. 30837

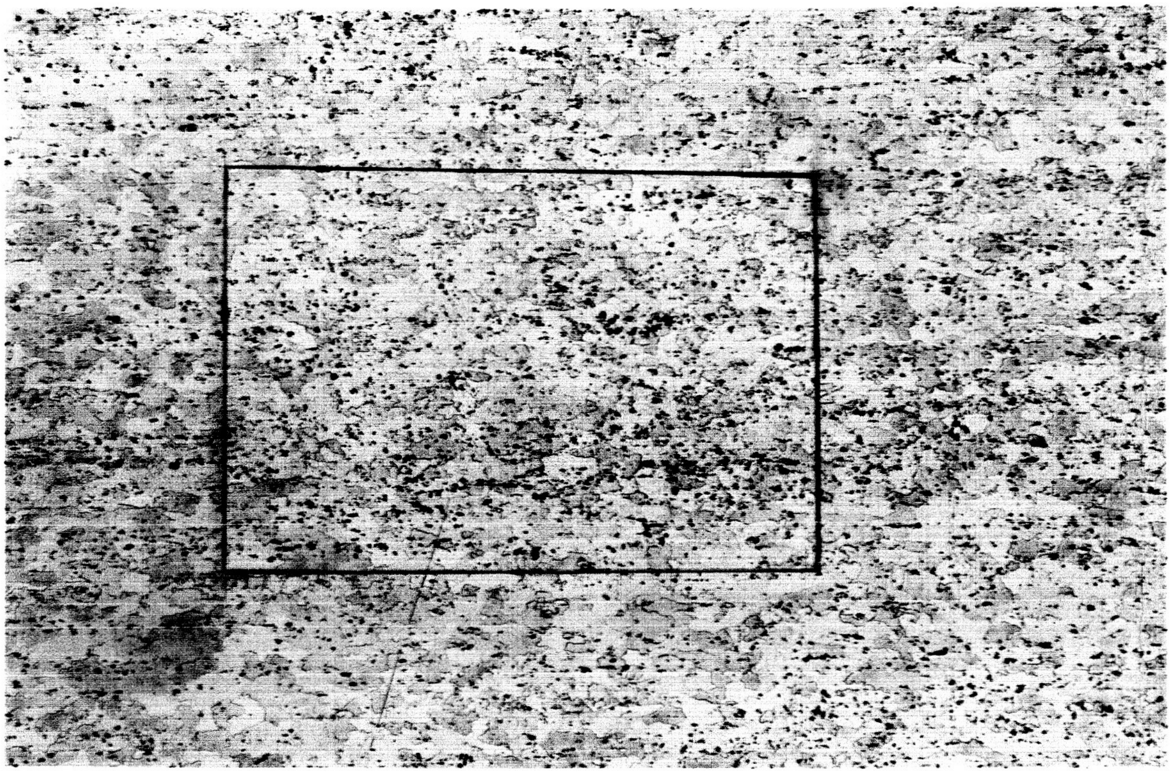
(c) Magnification 250X



Neg. No. 30838

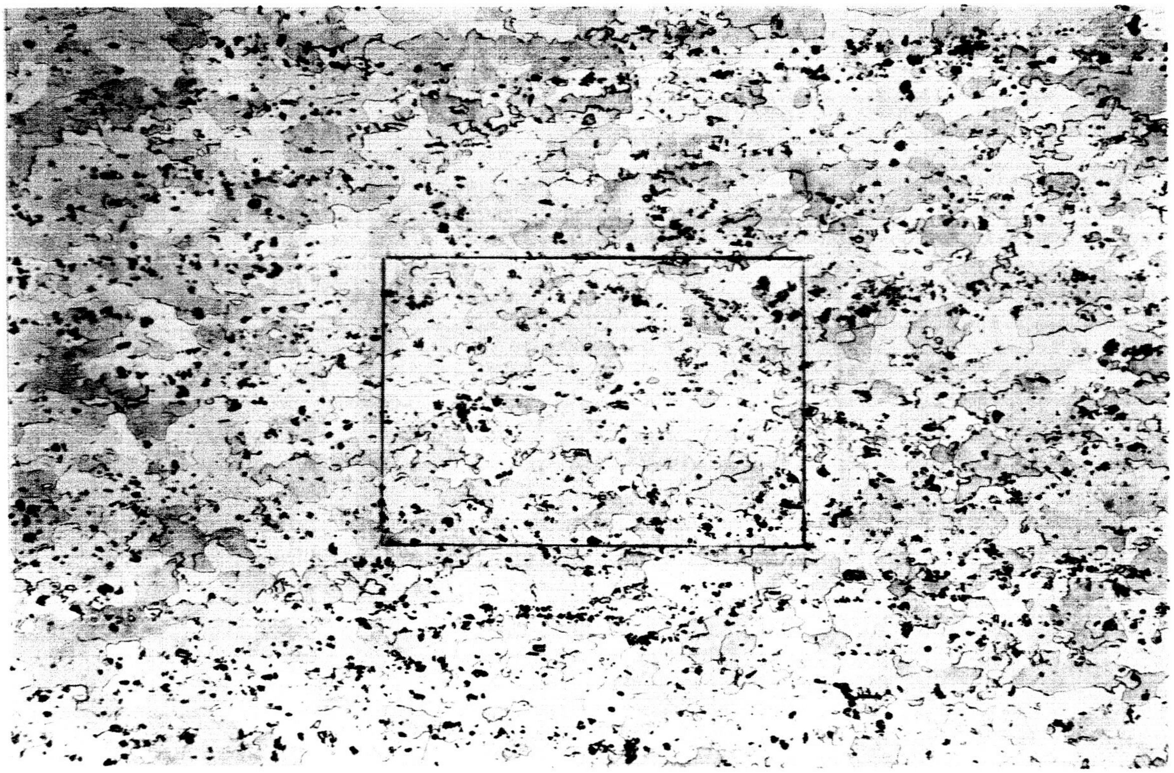
(d) Magnification 1000X

Fig. 26 (cont'd) - Structure of Type 2014-T451 Aluminum Before Chem-Milling.



Neg. No. 30886

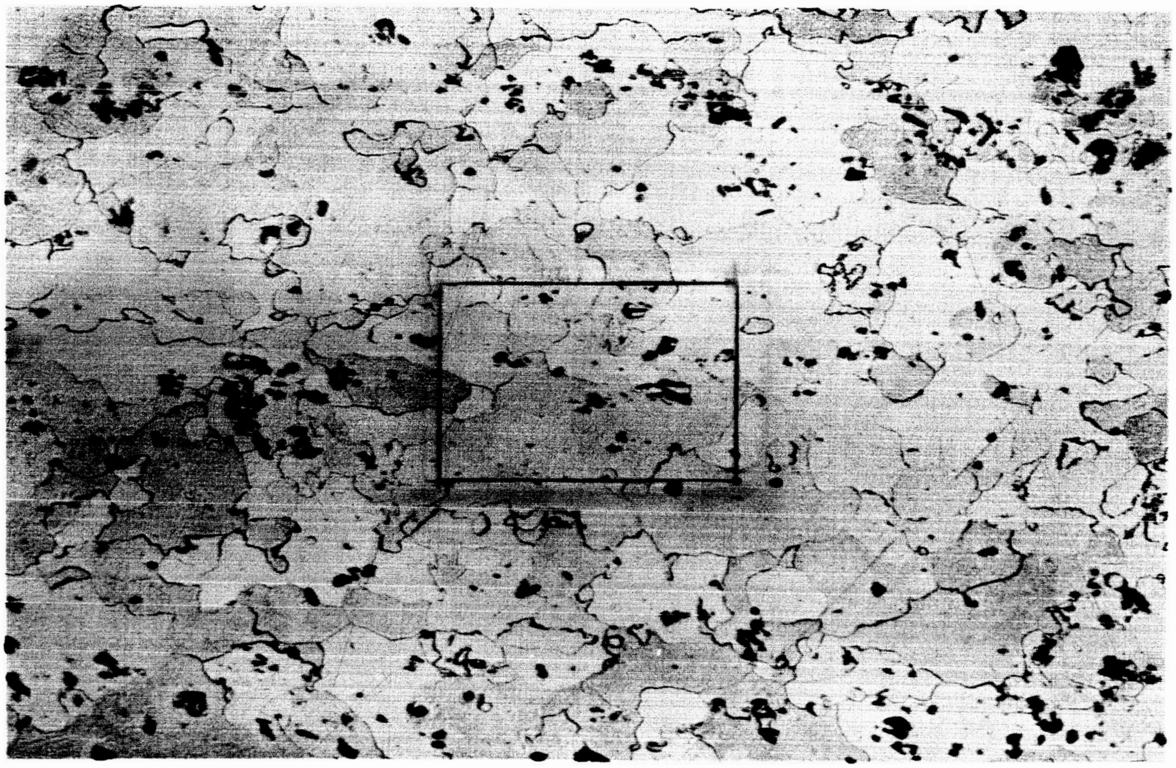
(a) Magnification 50X



Neg. No. 30887

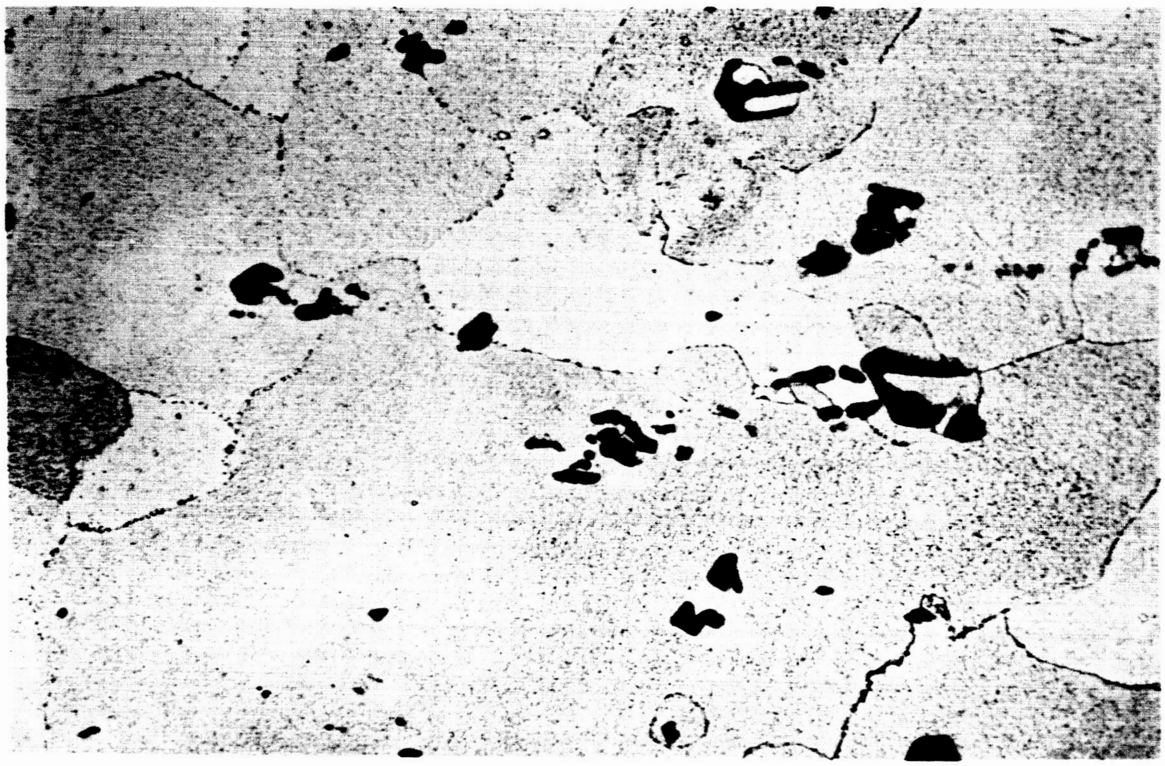
(b) Magnification 100X

Fig. 27 - Structure of Type 2014-T651 Aluminum Before Chem-Milling (Artificially Aged). Rectangles Show Area of Next Higher Magnification. Keller's etch.



Neg. No. 30888

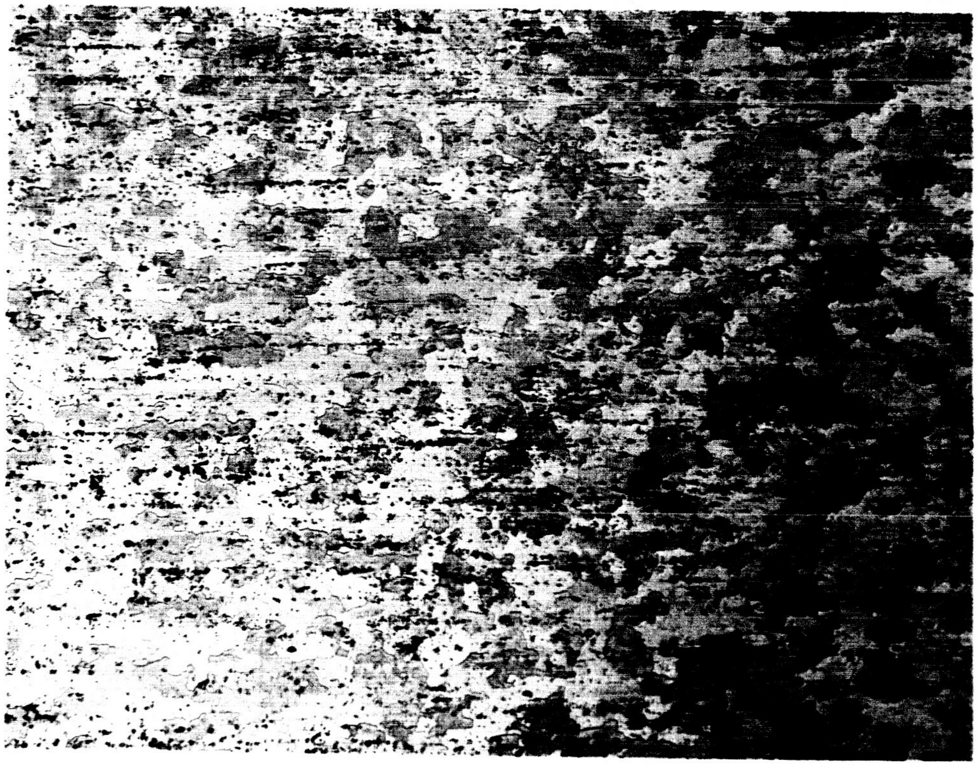
(c) Magnification 250X



Neg. No. 30889

(d) Magnification 1000X

Fig. 27 (cont'd) - Structure of Type 2014-T651 Aluminum Before Chem-Milling.



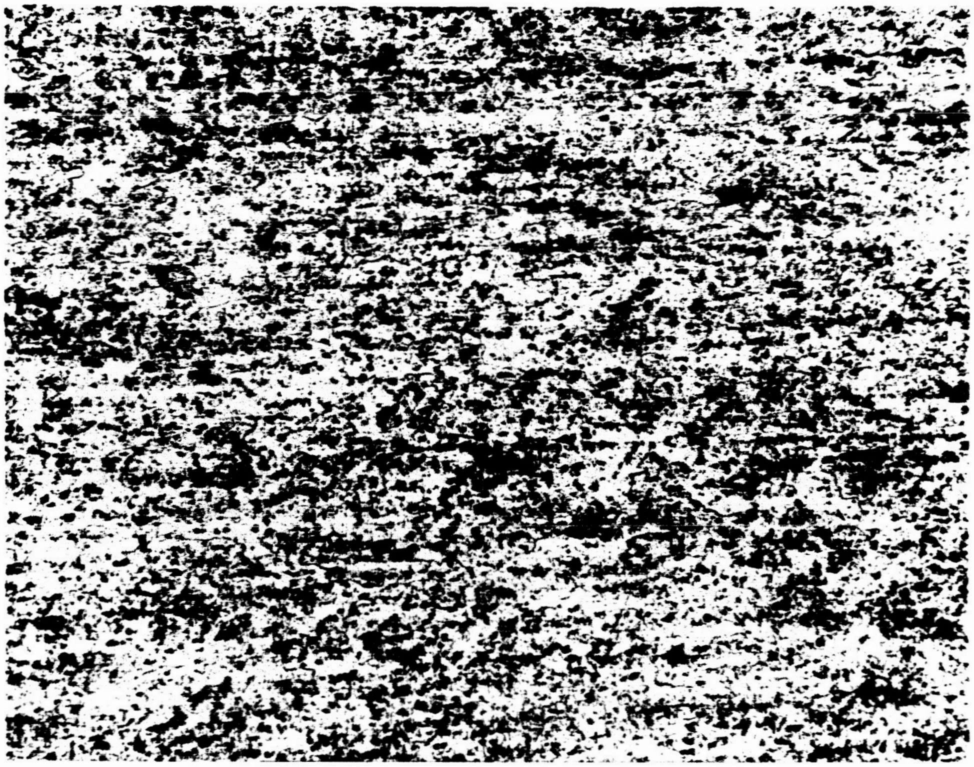
Neg. No. 30835 50X

(a) Original Surface

Neg. No. 30839 50X

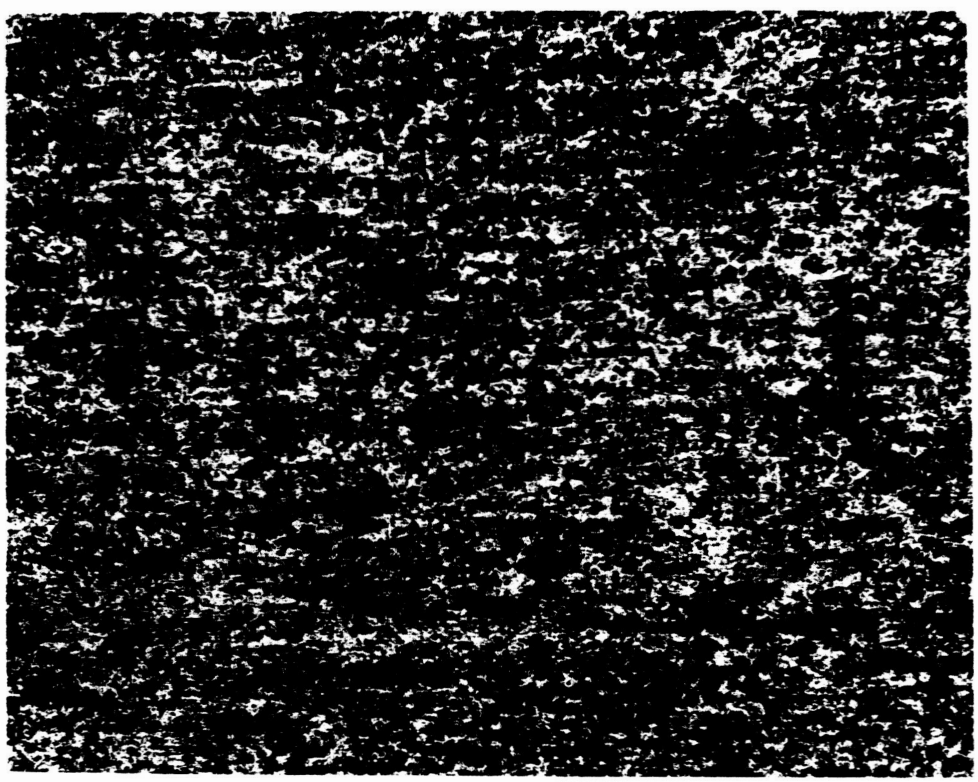
(b) 5 sec. etch

Fig. 28 - Chem-Milling Sequence for Type 2014-T451 Aluminum (Naturally Aged). All photographs are of the same area of the specimen. Etching medium: NaOH, 15 oz/gal, 190°F



Neg. No. 20846 50X

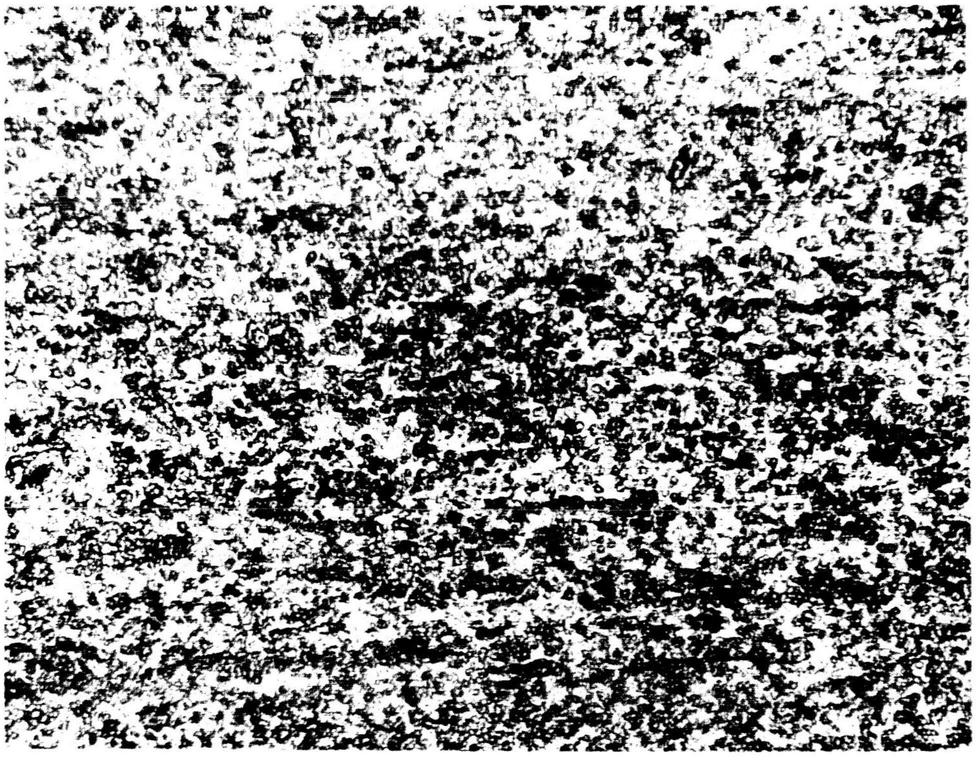
(c) 20 sec. etch



Neg. No. 30850 50X

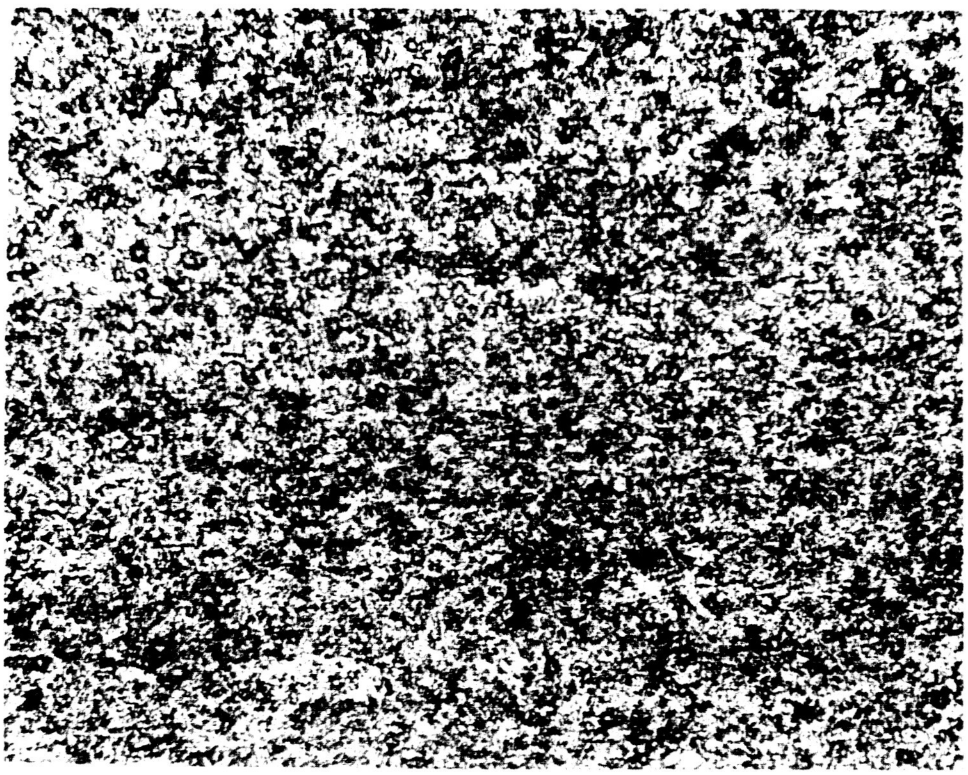
(d) 45 sec. etch

Fig. 28 (cont'd) - Chem-Milling Sequence for Type 2014-T451 Aluminum.



Neg. No. 30858 50X

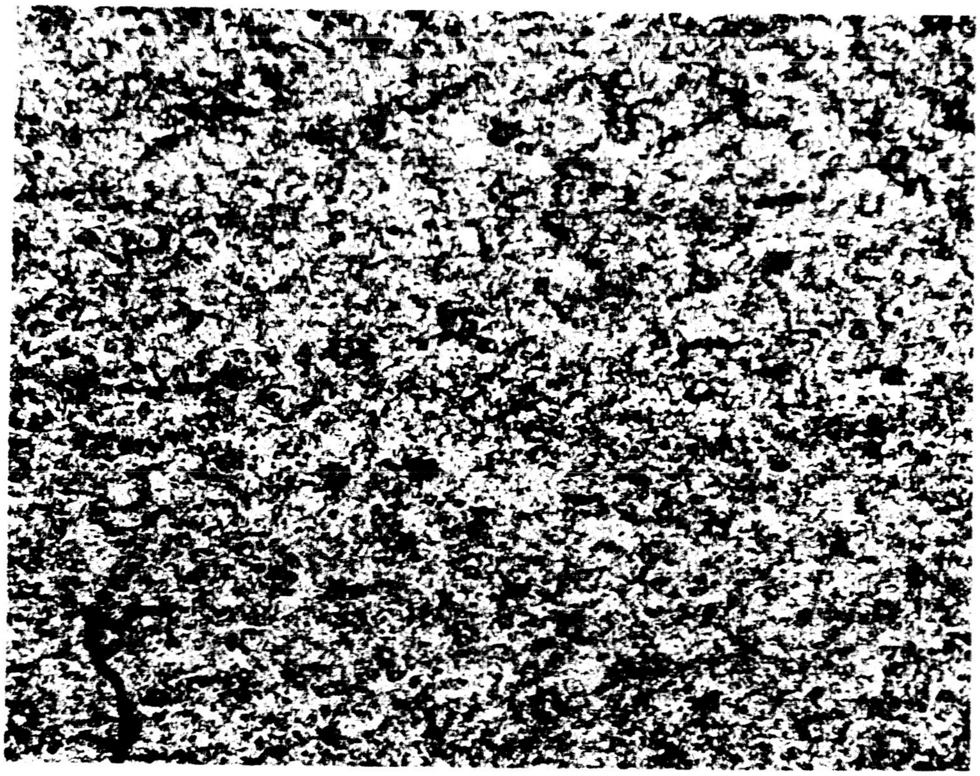
(e) 75 sec. etch



Neg. No. 30862 50X

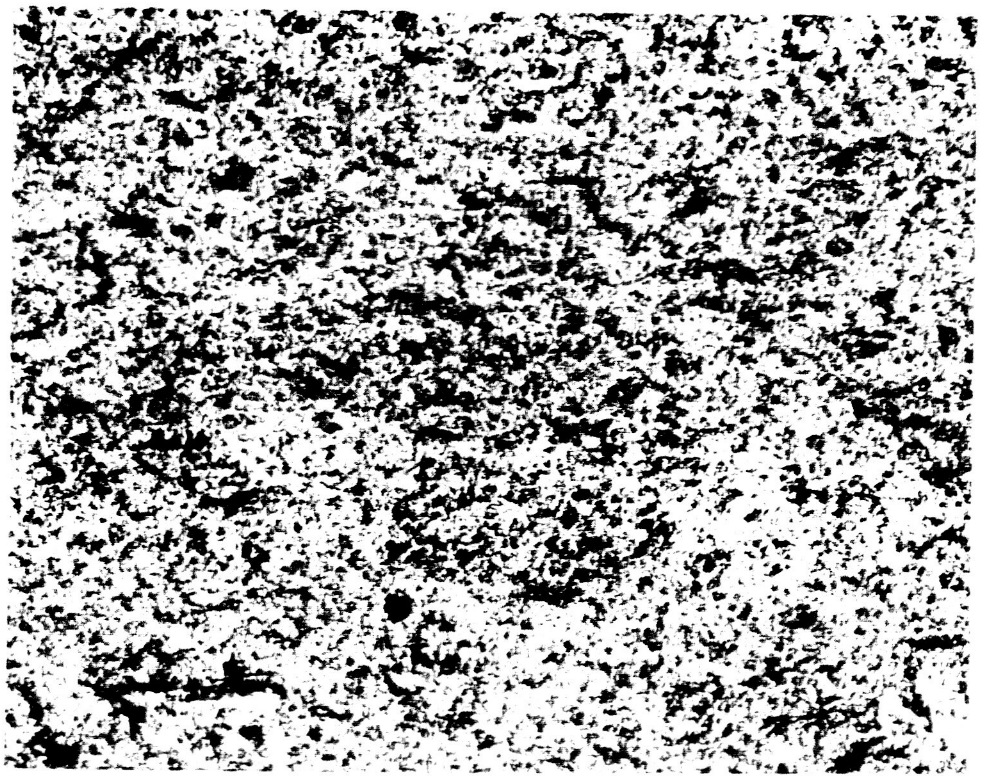
(f) 150 sec. etch

Fig. 28 (cont'd) - Chem-Milling Sequence for Type 2014-T451 Aluminum.



Neg. No. 30865 50X

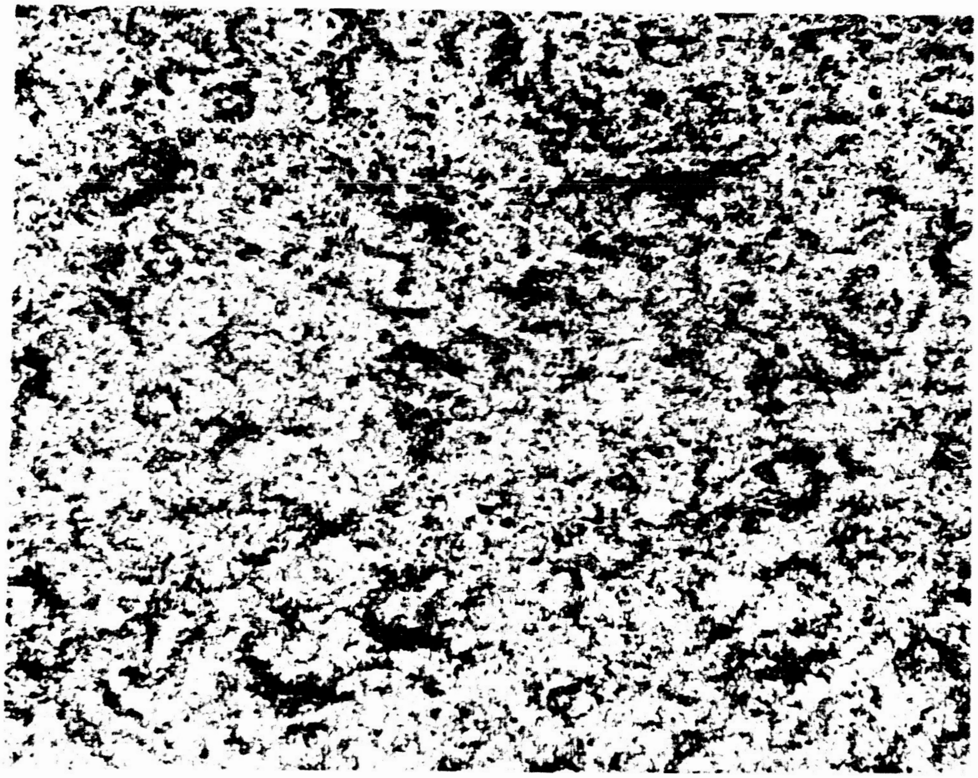
(g) 5 min. etch



Neg. No. 30868 50X

(h) 10 min. etch

Fig. 28 (cont'd) - Chem-Milling Sequence for Type 2014-T451 Aluminum.



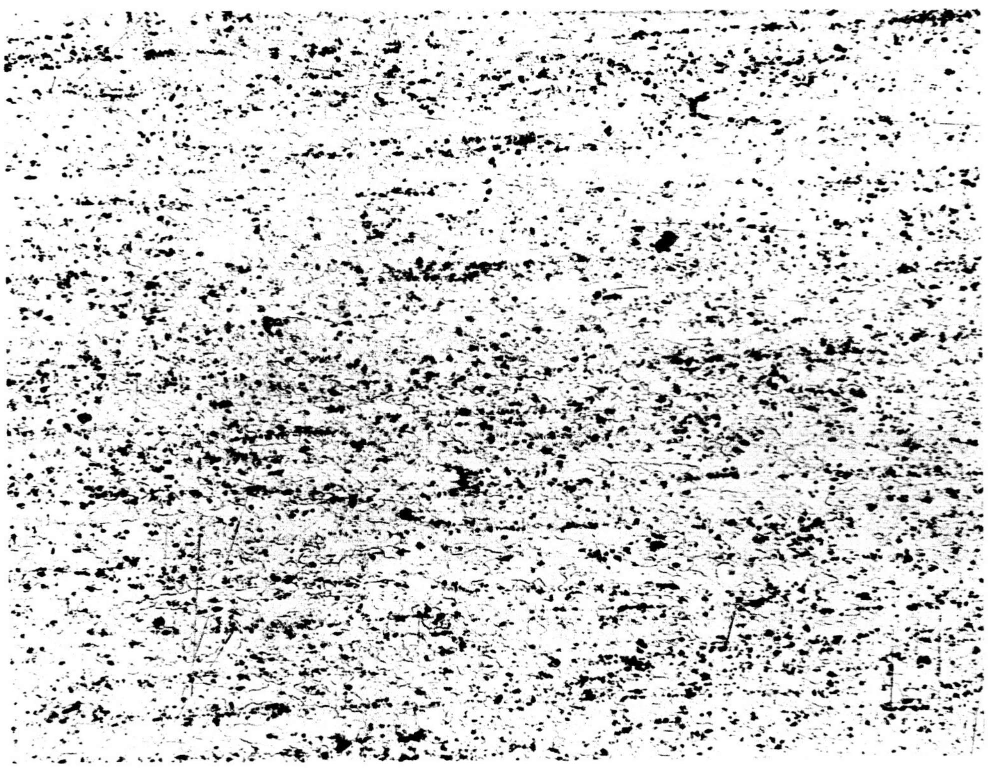
Neg. No. 30880 50X

(i) 15 min. etch

Fig. 28 (concluded) - Chem-Milling Sequence for Type 2014-T451 Aluminum.

Neg. No. 30886 50X

(a) Original Surface



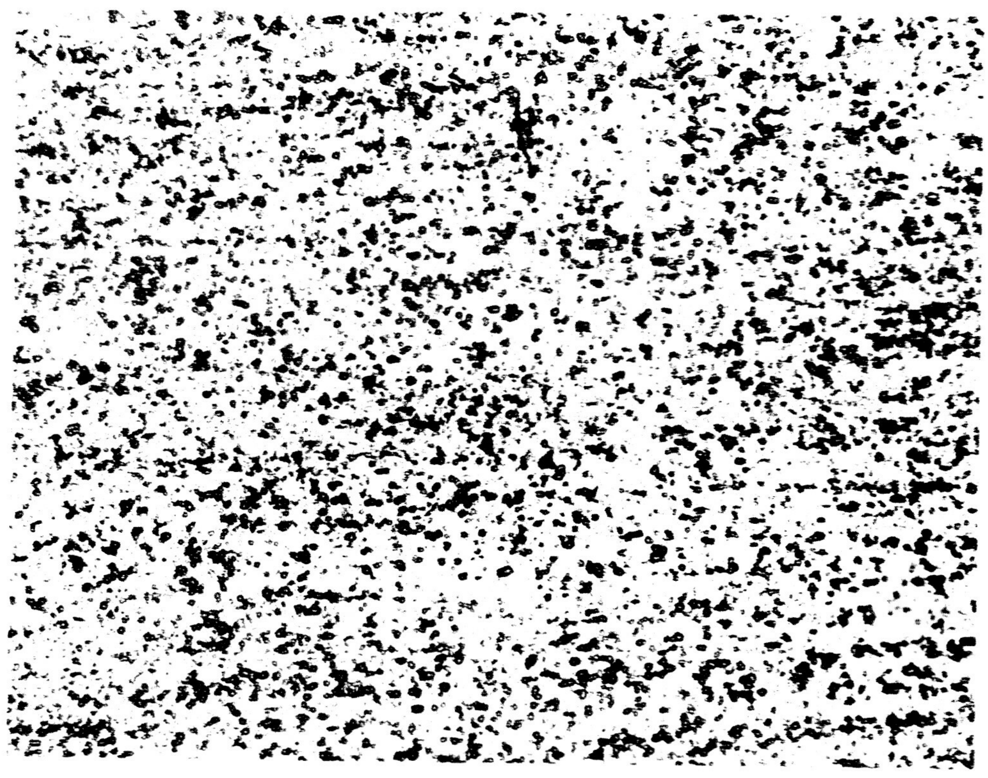
Neg. No. 30890 50X

(b) 5 sec. etch

Fig. 29 - Chem-Milling Sequence for Type 2014-T651 Aluminum (Artificially Aged). All photographs are of the same area of the specimen. Etching Medium: NaOH, 15 oz/gal, 190°F.

Neg. No. 30919 50X

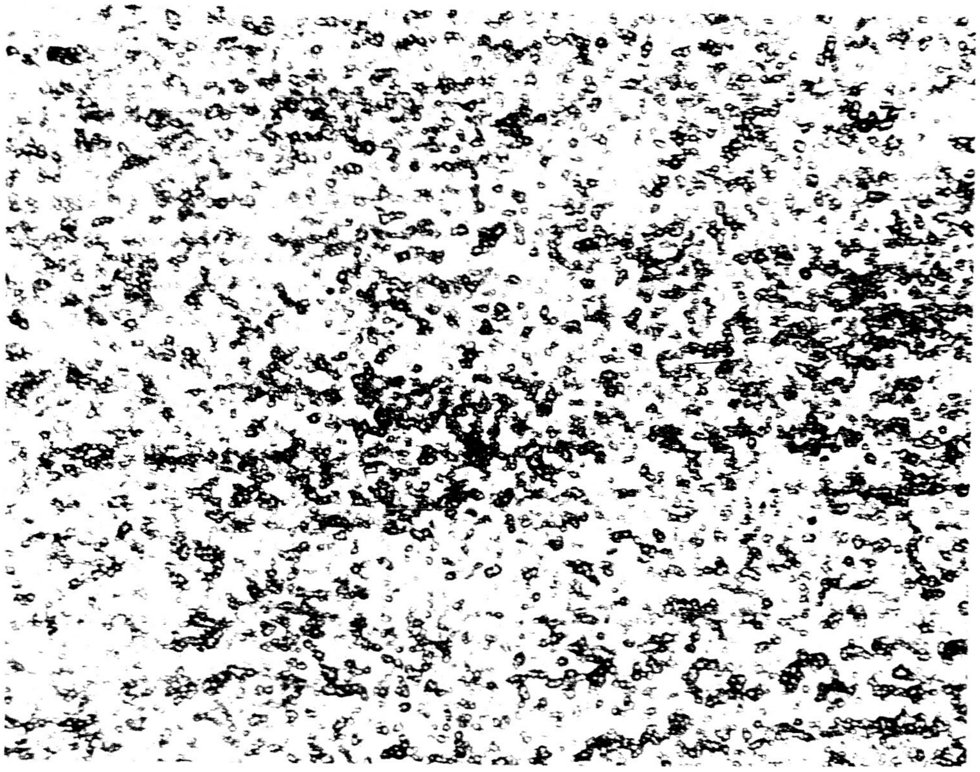
(c) 20 sec. etch



Neg. No. 30940 50X

(d) 45 sec. etch

Fig. 29 (cont'd) - Chem-Milling Sequence for Type 2014-T651 Aluminum.



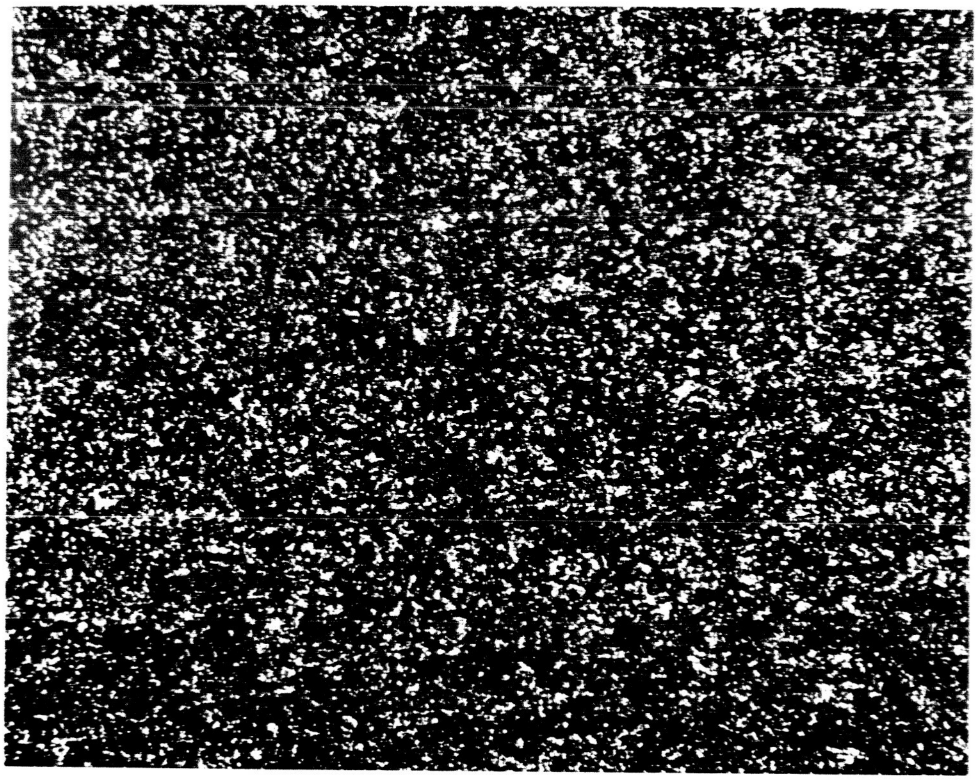
Neg. No. 30944 50X

(e) 75 sec. etch

Neg. No. 30955 50X

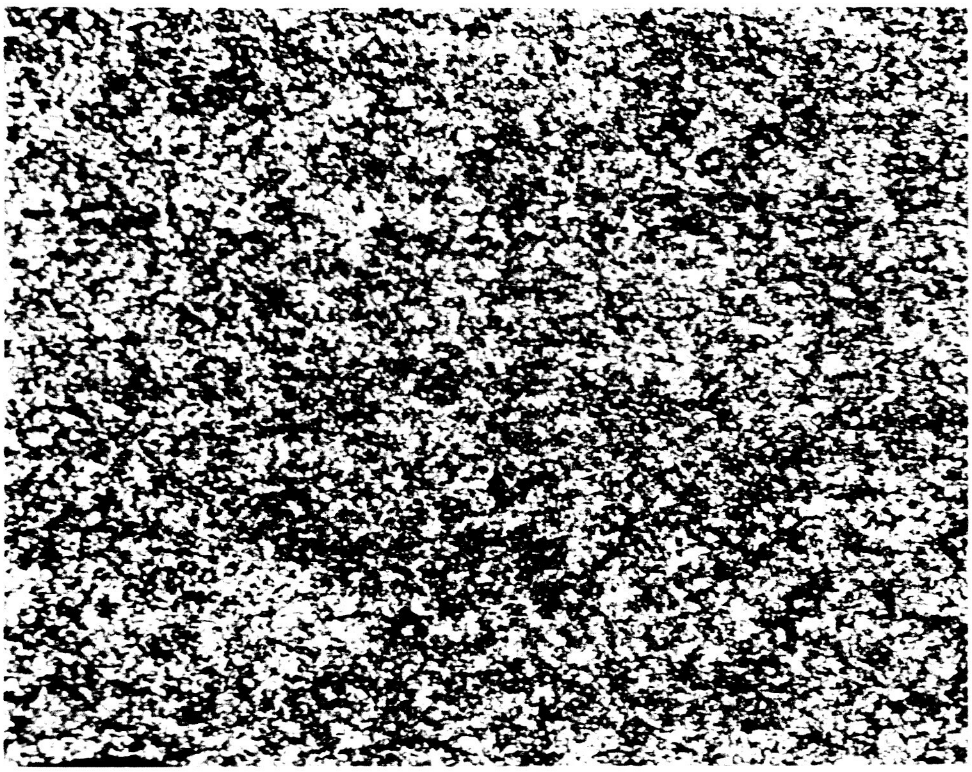
(f) 150 sec. etch

Fig. 29 (cont'd) - Chem-Milling Sequence for Type 2014-T651 Aluminum.



Neg. No. 30960 50X

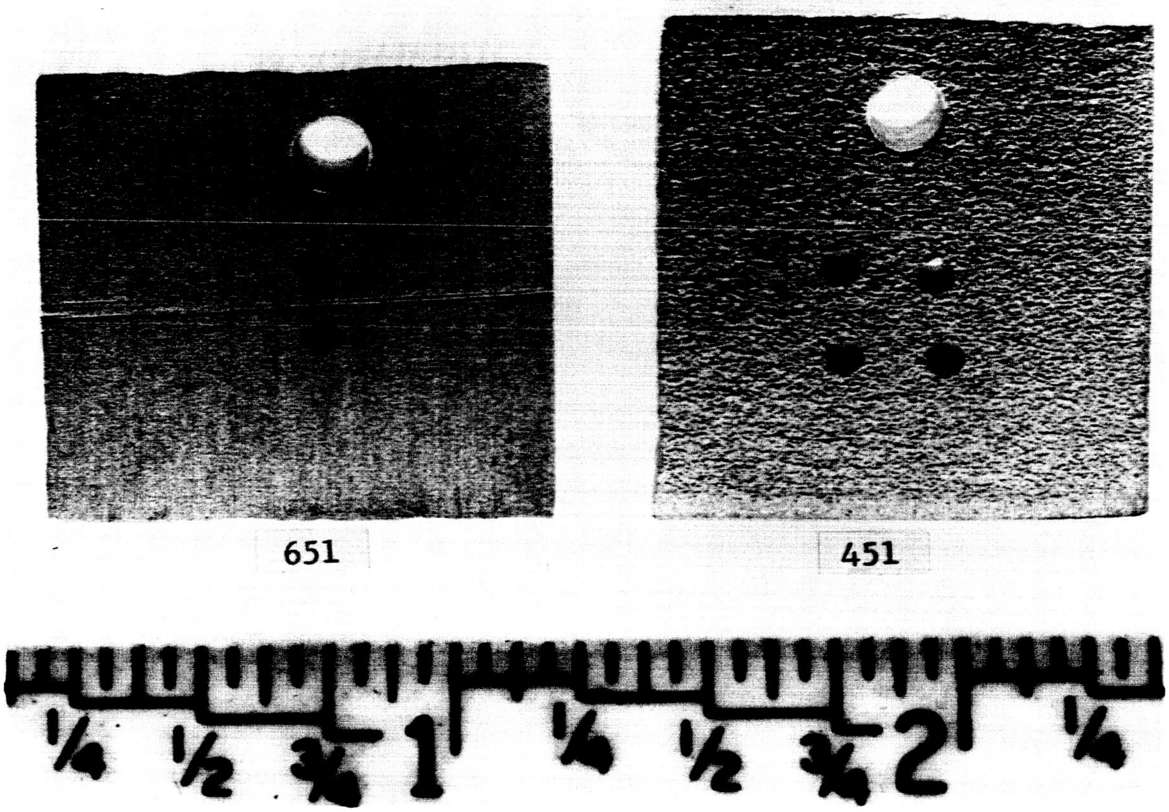
(g) 5 min. etch



Neg. No. 30964 50X

(h) 10 min. etch

Fig. 29 (concluded) - Chem-Milling Sequence for Type 2014-T651 Aluminum.




Neg. No. 30996

Fig. 30 - Surfaces of Specimens of Type 2014-T451 and 2014-T651 Aluminum after Etching Sequences of Figures 28 and 29.

## H. Conclusions

The rough etching displayed by Type 2014-T451 aluminum is simply a characteristic of that aging condition, and is not due to defects in the manufacturing sequence.

There is evidence to show that there is probably an effect of composition on the degree of roughness produced when the alloy is milled in the T4 condition, but certainly not enough information is available to decide which elements are particularly important. This could be determined by a thorough study of the etching of a large number of lots of 2014 material, together with a statistical correlation of the etching properties with the chemical composition of each lot. The problem seems most easily solved, however, by simply performing all chem-milling of 2014 alloy while it is in the artificially aged condition (T6).

It is clear from the studies performed that the roughness that develops during etching of the T4 material is not directly related to corresponding microstructural zones. Instead, it appears that the type 2014-T451 material simply undergoes what might be called "spontaneous separation" of anodic and cathodic zones. That is, as etching proceeds, the cathodic activity tends to increase in certain areas, while the anodic activity tends to concentrate in other areas. These zones are of "macro" dimensions, seemingly unrelated to the "micro" structure of the metal. When this segregation of electrochemical function occurs, the anodic zones, of course, suffer intensified attack and are the sites of pit development.

In the artificially aged material, however, this effect seemingly does not occur. Instead all zones tend toward an equal distribution of anodic and cathodic sites. Not only is there this tendency toward establishing "electrochemical homogeneity," but this equalized distribution appears to be the stable dynamic condition. Thus, if a slight nonuniform attack occurs locally on the metal, it seems that there is a "self-restoring" tendency, the result of which is an increase in rate of attack on high spots and, therefore, a smoothing effect.

## VI. STUDIES OF TYPE 7075 ALUMINUM

### A. Aging Experiments

As with Type 2014 alloy, the difficulty frequently met in chem-milling Type 7075 aluminum is surface roughness. Of the materials provided for study in the present program, one lot of Type 7075 alloy was received in the -0 temper, while one was 7075-T6. The latter material showed very smooth etching in sodium hydroxide, while the former showed considerably rougher etching, at first thought to be related to the larger grain size of that material.

Recalling the effects of quenching rate and aging treatments on the milling properties of Types 2219 and 2014, the experiment of Figure 31 was planned for Type 7075. In the categories (a) to (e), specimens were milled for various times in NaOH (15 oz/gal at 190°F) to observe the tendency toward development of roughness. The conditions included "W" (solution annealed and quenched) as well as three different aging treatments for one lot of 7075, while the other lot was milled in the T6 condition. Thus, group "b" and "e" are nominally the same except that they are from two different lots of aluminum.

The response to milling was judged visually and by a "proficorder" measurement at 0, 5, 10, and 15 min. of milling. The results are shown in Figures 32-36, where the proficorder records are shown for each specimen and at each time period. In each tracing, the total distance along the trace is about 0.2 in., while the roughness scale is 100 microinches/division.

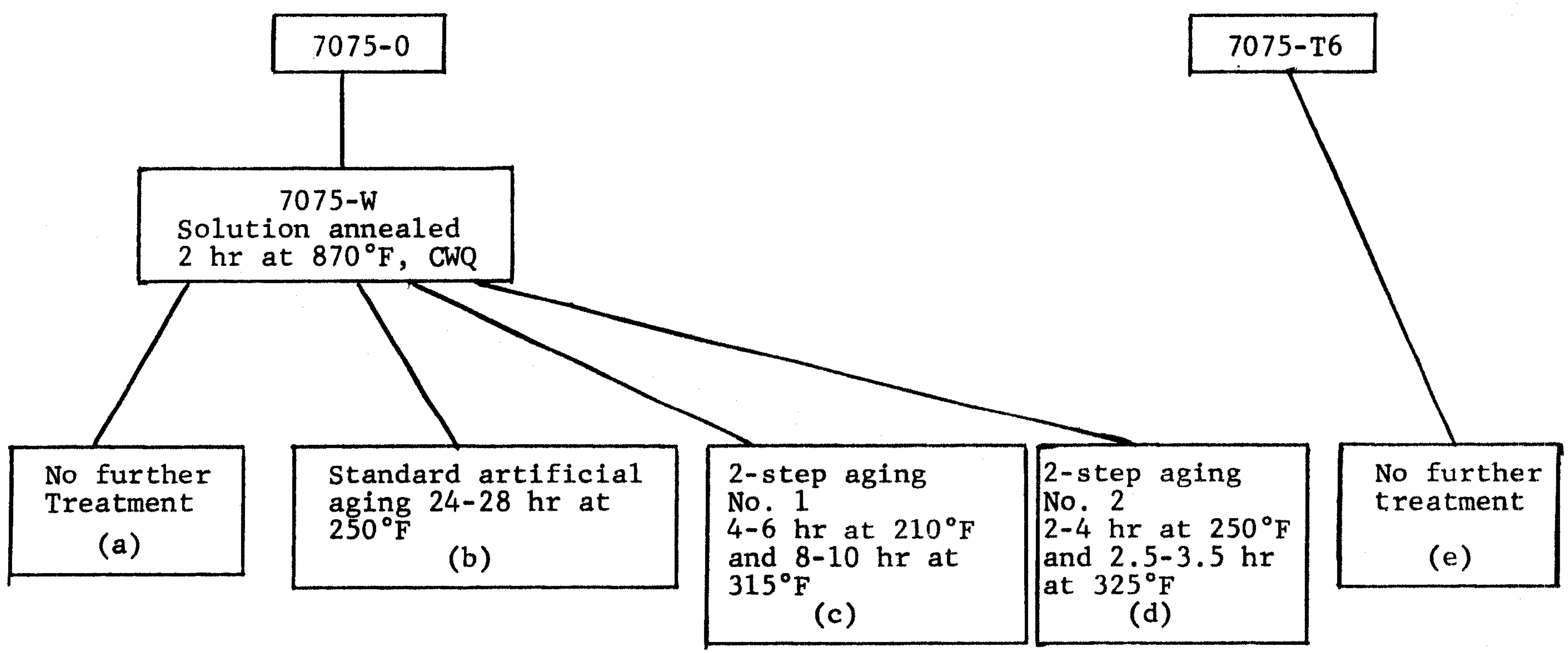
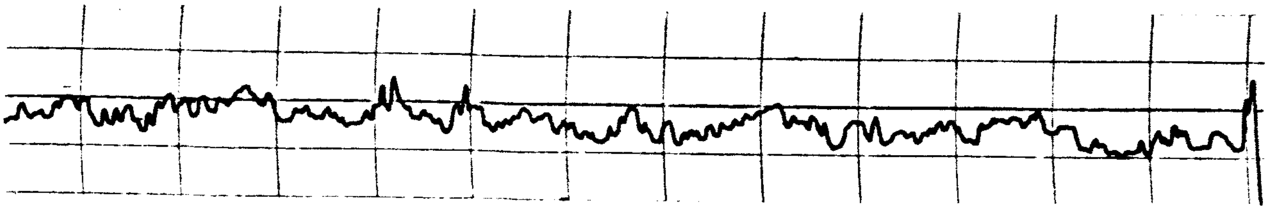
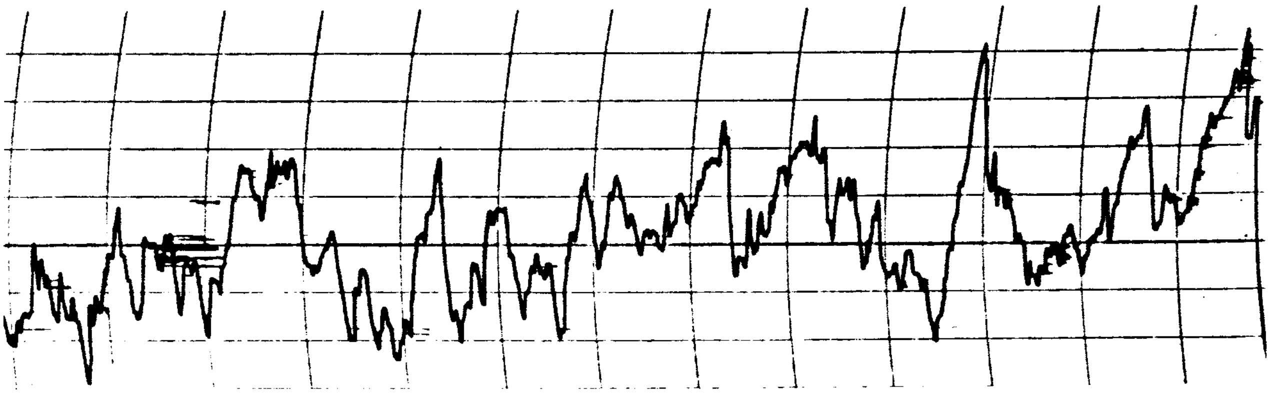


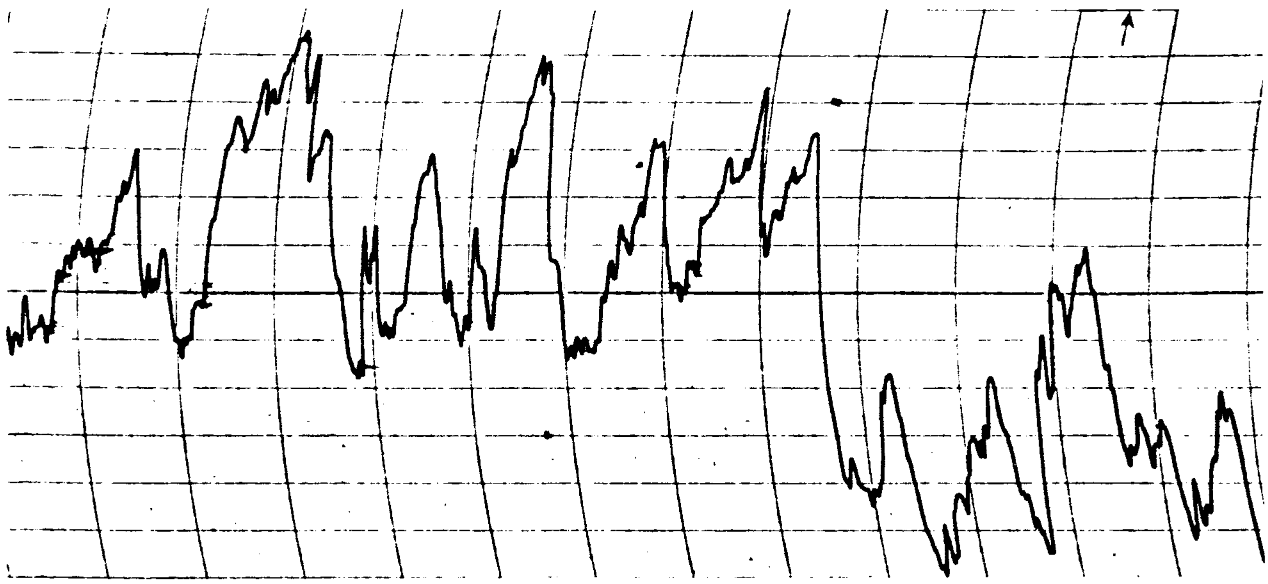

Fig. 31 - Aging Study on Type 7075 Aluminum.



0 min.

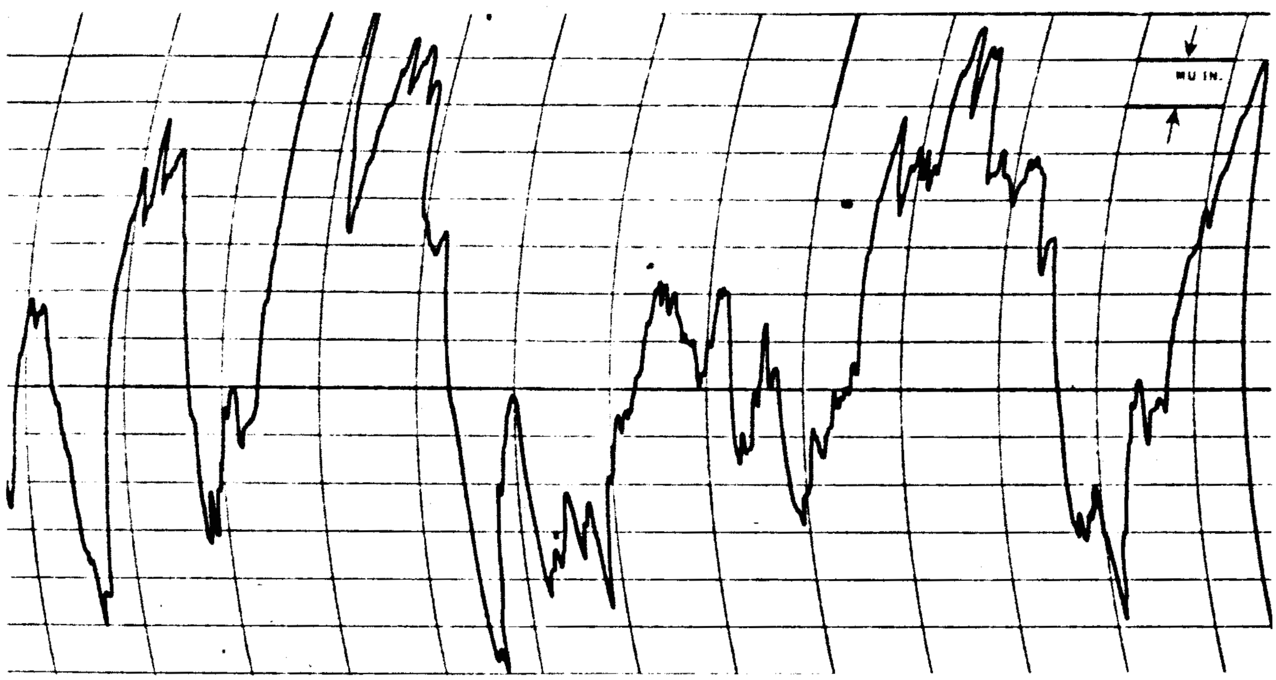


5 min.



10 min.

Fig. 32 - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series(a)of Figure 31.




15 min.

Fig. 32 (cont'd) - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series (a) of Figure 31.

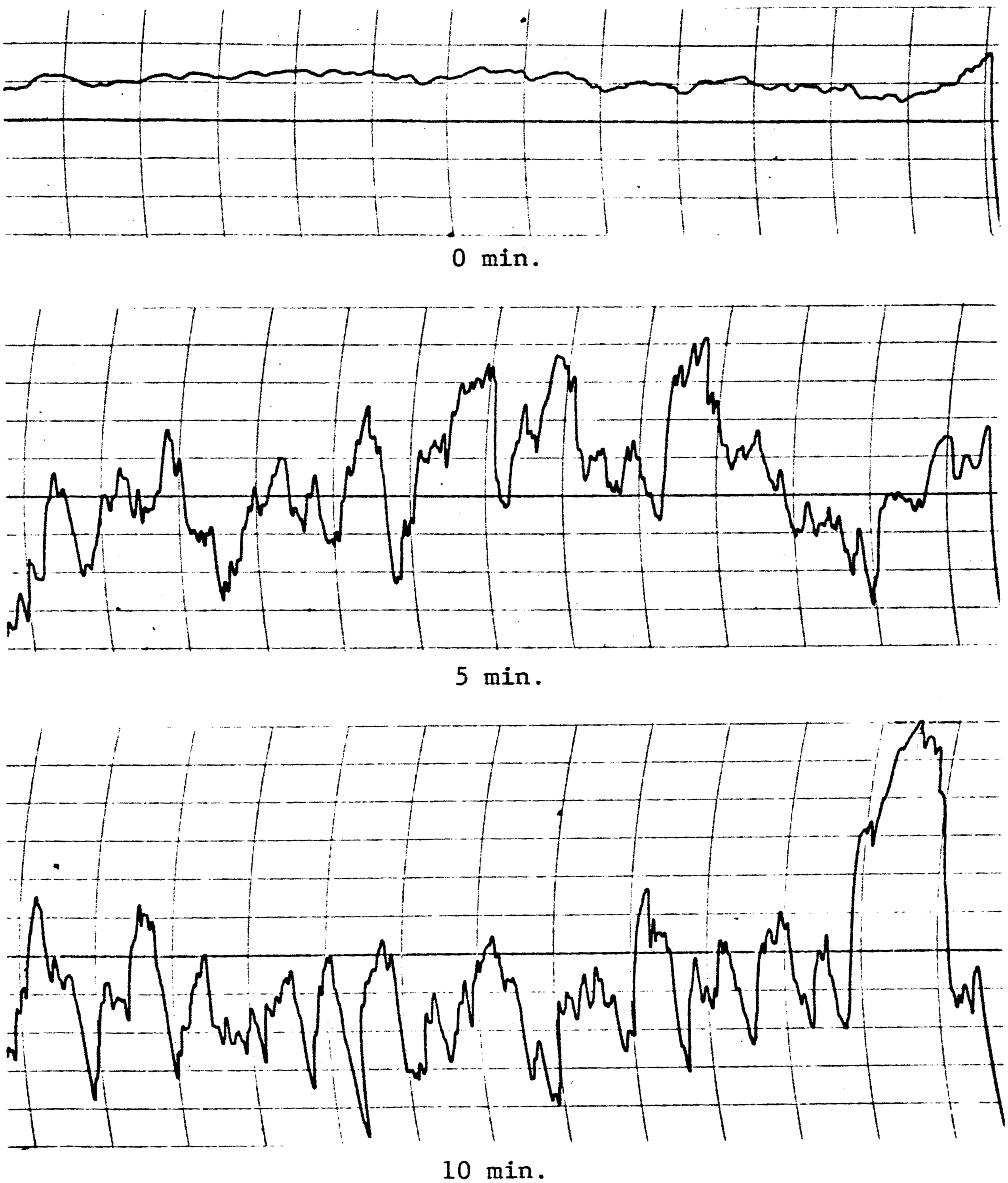
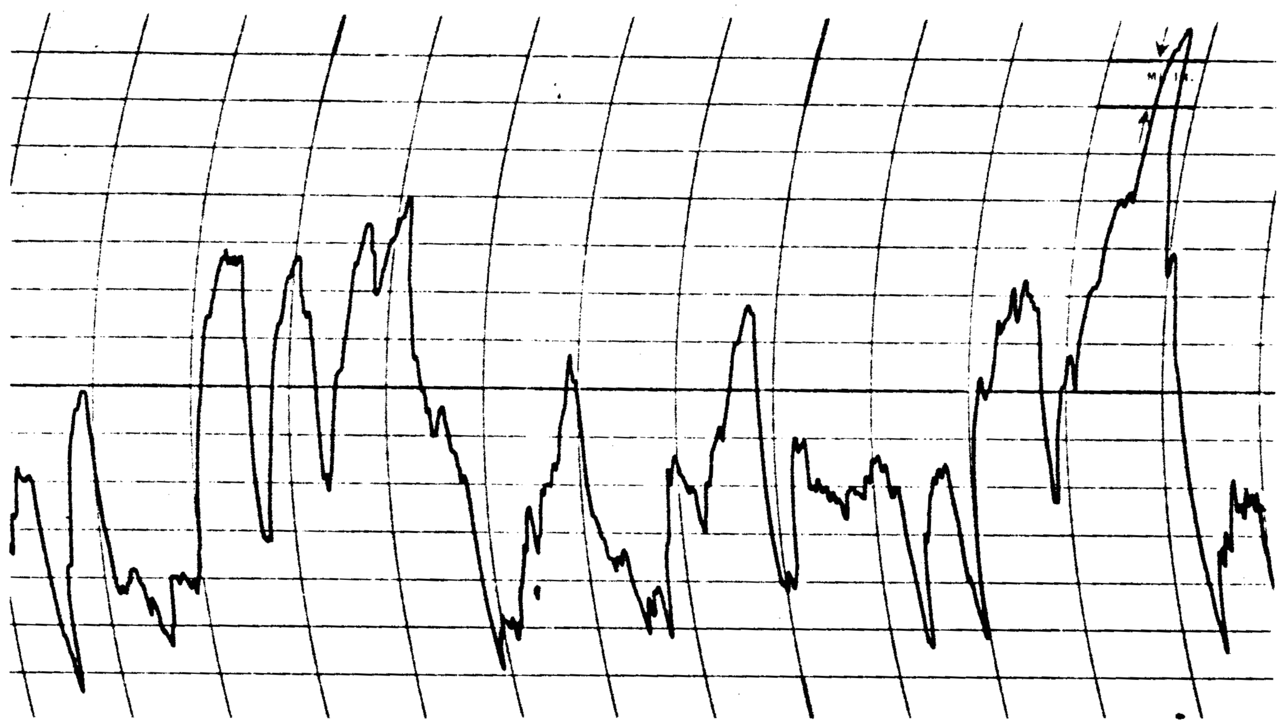
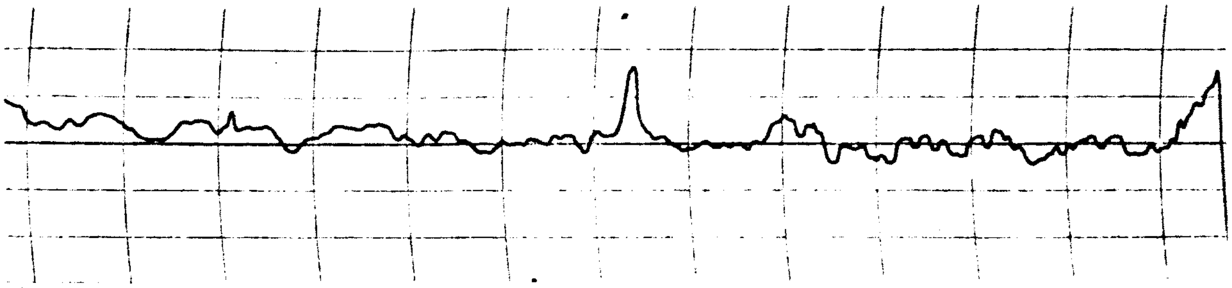



Fig. 33 - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series (b) of Figure 31.

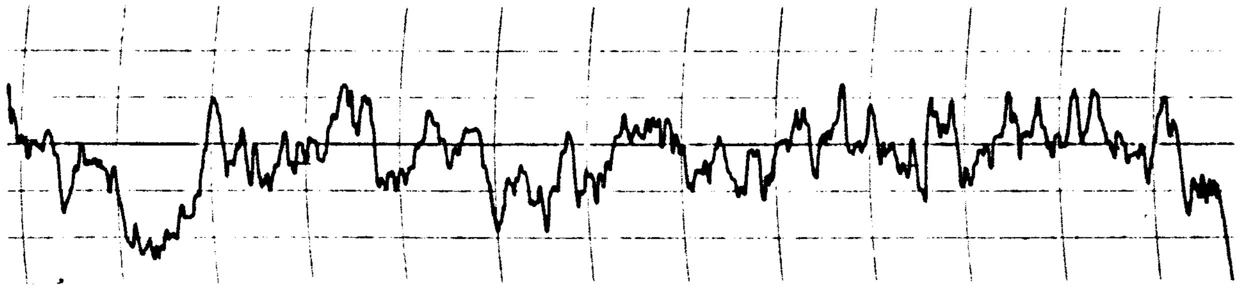


15 min.

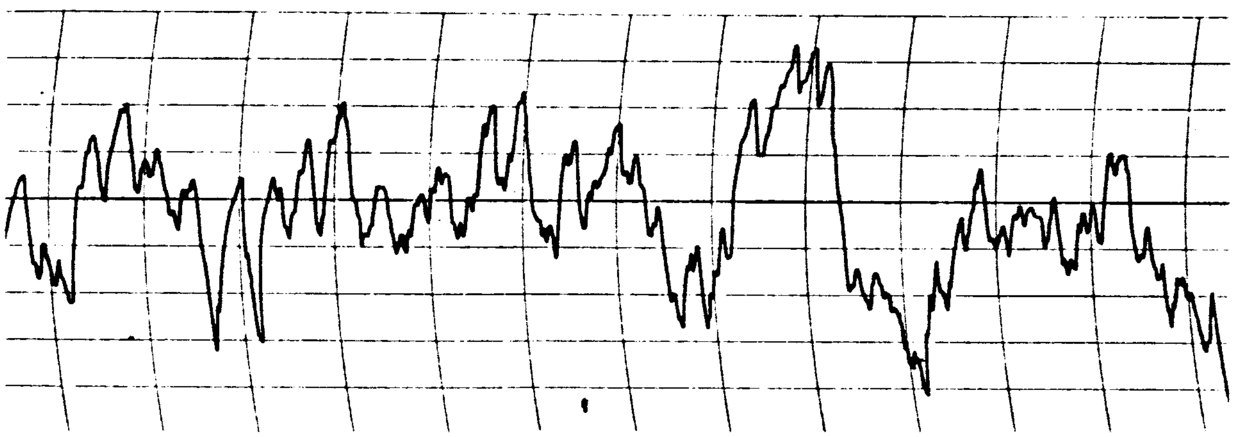
Fig. 33 (cont'd) - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series(b)of Figure 31.



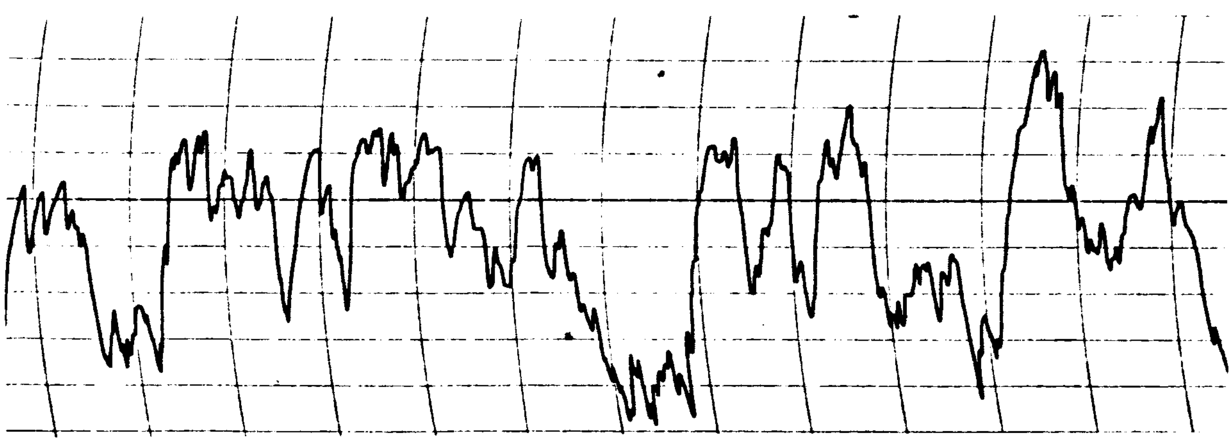
0 min.



5 min.



10 min.



15 min.

Fig. 34 - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series(c)of Figure 31.

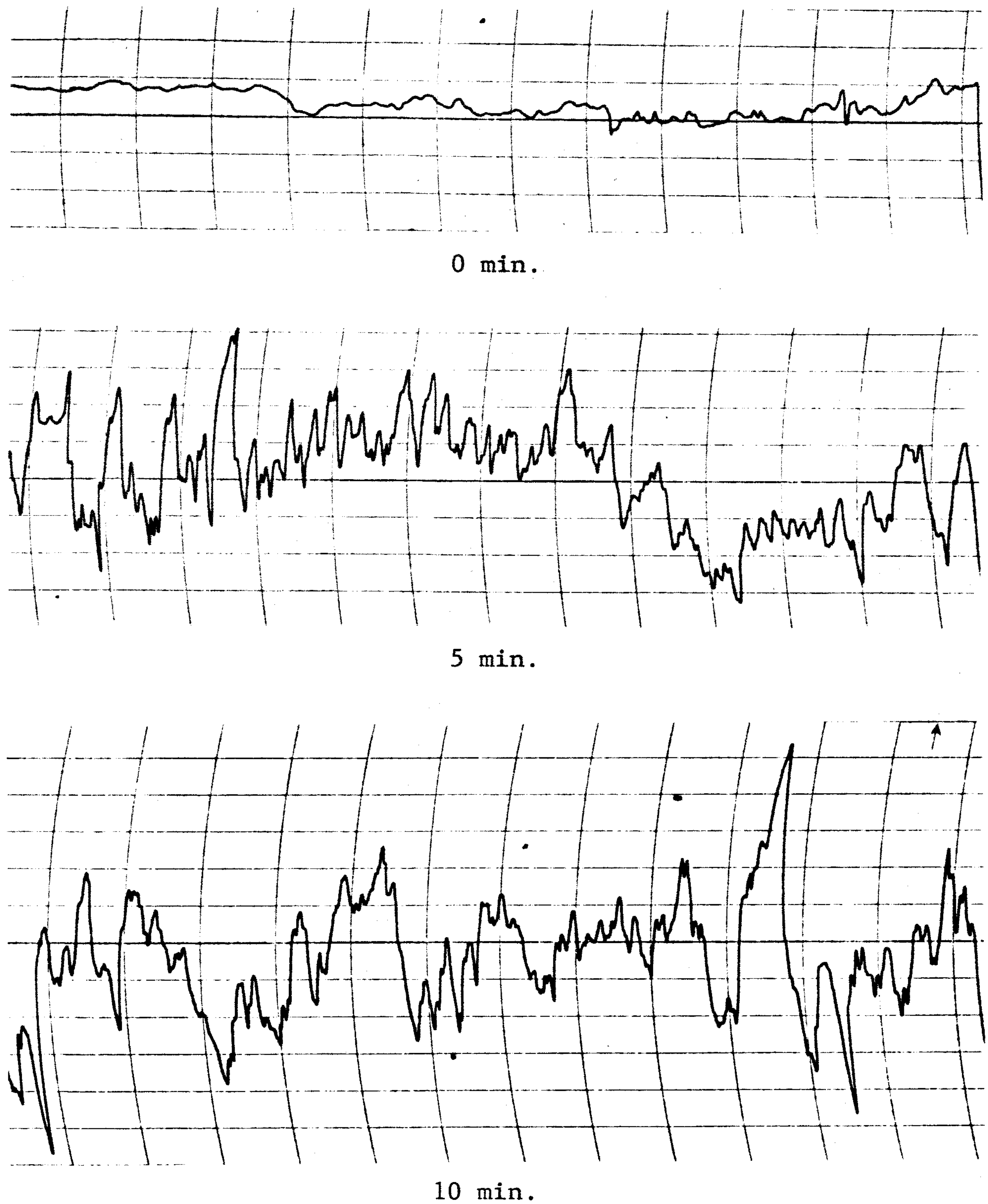
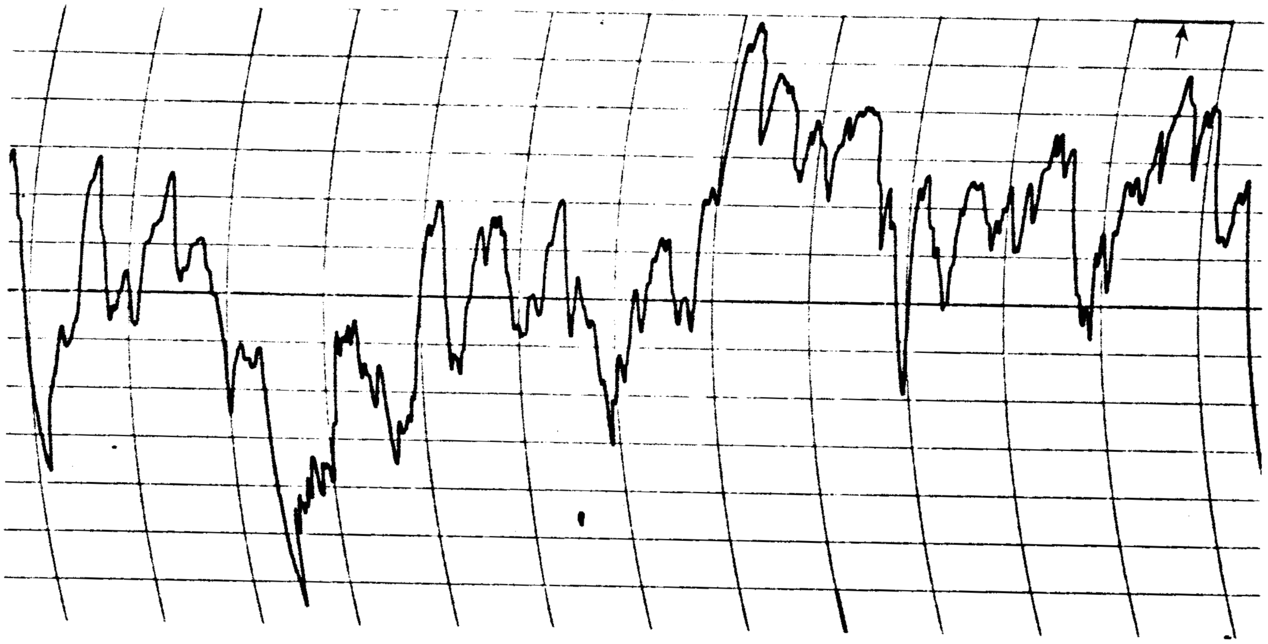
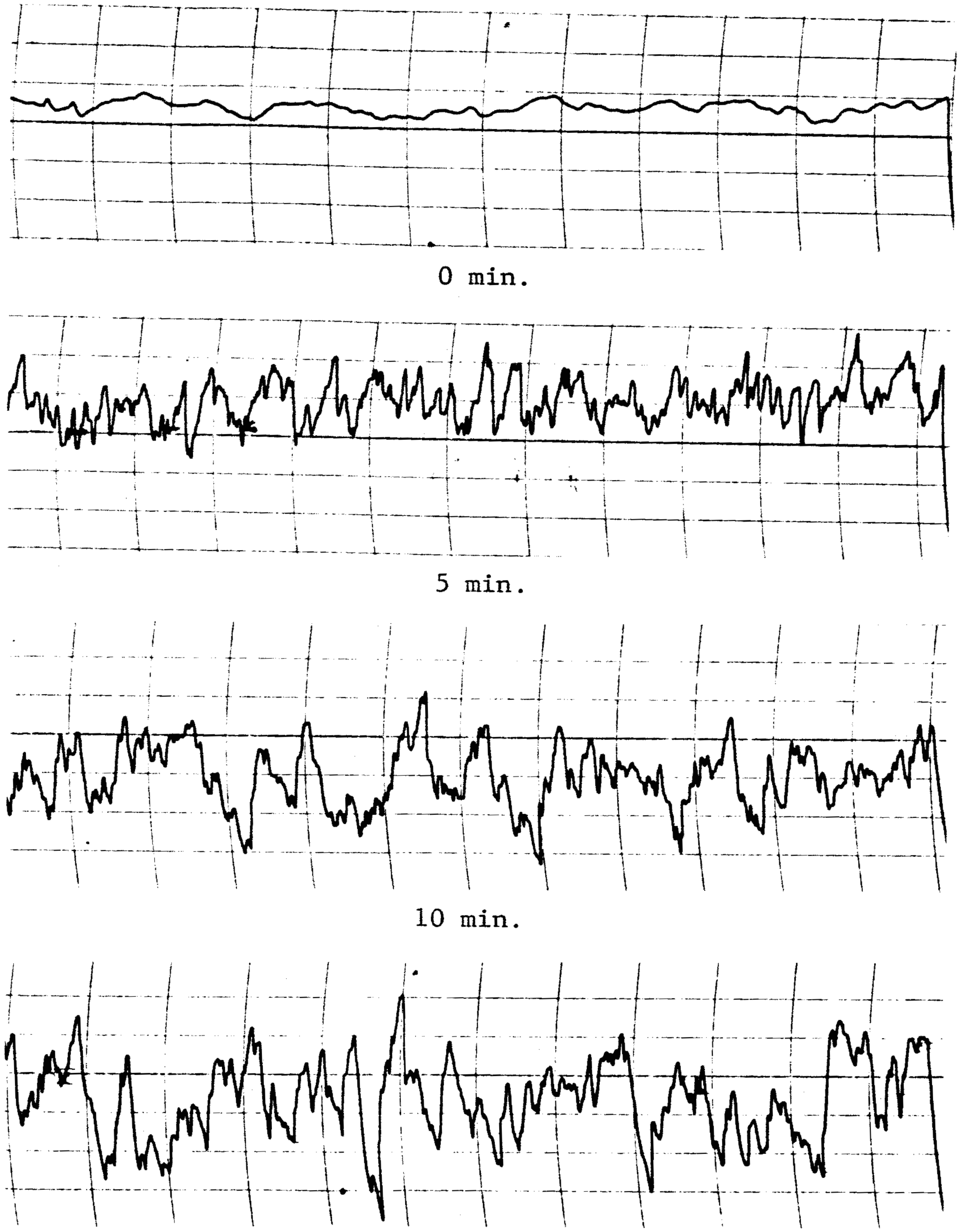



Fig. 35 - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series(d)of Figure 31.



15 min.

Fig. 35 (cont'd) - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series(d)of Figure 31.



0 min.

5 min.

10 min.

15 min.

Fig. 36 - Proficorder Records During Chem-Milling of Type 7075 Specimens from Series(e)of Figure 31.

It is clear from the records that the as-received Type 7075-T6 (series e) shows quite the smoothest milling. This was confirmed visually. Of the several variations on this lot of alloy that was received in the -0 condition, series c and d were certainly smoother than a or b, but not as smooth as e.

Thus, the conclusion must be drawn that the variations in Type 7075 alloy must be due, at least in part, to compositional or structural differences in the original lot of material, and not due primarily to heat-treatment variations.

Confirmation of this view was found when metallographic examination was made of (nominally) identical specimens taken from series b and e of Figure 31. The micrographs are shown in Figure 37. The conclusion is evident that the two lots of alloy are quite comparable in terms of grain size and degree of recrystallization. The sample from series b, however, clearly shows a great deal more dark-etching precipitate than does the sample from series e. Just how this structural difference causes the one lot to etch rough while the other etches smooth is not clear of course, but at least it is consistent with the apparent random nature of the occurrence of rough etching in Type 7075 alloy.

## B. Conclusions

The roughness met occasionally in chem-milling Type 7075 aluminum is apparently due to a truly "random" variation in the parent metal. That is, within the allowable limits of compositional variation and within usual limits of variation in grain-size and other metallographic features, it is nevertheless possible to have conditions which favor development of roughness during chem-milling. Of the four alloys studied, Type 7075 yielded the least meaningful results with respect to corrective measures whereby roughness might be avoided. Apparently, the factors that eventually determine the milling

Neg. No. 30882 20 sec. Keller's etch, X100

Sample from Series(b)

Neg. No. 30883 20 sec. Keller's etch, X100

Sample from Series(e)

Fig. 37 - Structure of Specimens of Type 7075 Aluminum from Figure 31.

characteristics of a given lot of alloy are determined well back in the history of the material. It may go back to the original melt composition, or only as far as the casting of the ingot from the melt. At any rate, the conditions at this point appear to determine eventual chem-milling properties. Furthermore, these conditions are not erased by a solution treatment--which is certainly the most "homogenizing" treatment available--short of remelting.

We must conclude, therefore, that rough etching in Type 7075 is still not understood well enough to permit recommendations for corrective measures.

## VII. CONDITIONS REQUIRED FOR SMOOTH CHEMICAL MILLING

It is perhaps appropriate at this point to inquire in a general way concerning the requirements for acceptably smooth chemical milling. Basically, it is this: At any given time in the milling process, the quantity of material removed per unit area should lie within certain limits for the entire surface being milled. The "quantity removed per unit area" is, of course, quite arbitrary, as is the "unit area." In practice, it has been found reasonable to specify the allowable maximum rms roughness for a chem-milled surface and the allowable dimensional variation from high to low points on the workpiece.

Let us inquire into the electrochemical factors that determine whether or not a given metal-etchant combination will yield acceptably smooth and uniform stock removal.

### A. The Metal

First of all, the removal of aluminum by an alkaline chem-milling medium is an example of one of the most vigorous electrochemical "corrosion" reactions known. There is little doubt that the reaction is electrochemical, since the cathodic and anodic functions can be demonstrated to occur at "local" cathodes and anodes, respectively. What then determines if attack is to be uniform or rough? A look at experience in the field of "normal" corrosion will give a better picture of just what we are asking of the chem-milling process.

In a short but classic paper entitled "The Ubiquity of Localized Corrosion," Mears* pointed out that most corrosion processes lead to nonuniform attack on the metal. In fact, only when very special conditions obtain can one expect smooth general attack.

If a local zone of the metal is anodic, while the rest of the metal surface is cathodic, we will observe the phenomenon of "pitting." At the opposite extreme, if there is a local zone that is predominantly cathodic, while the remaining area is anodic, we will observe formation of a high spot or "bump" as attack progresses. Between these extremes, there may be any combination of anodic and cathodic areas.

In the chemical milling of aluminum alloys--and particularly in the high-strength materials of the present study--we can expect to find strong cathodic and anodic elements distributed more or less uniformly throughout the metal. When such an alloy is immersed in a chem-milling etchant, local action will take place between all of these elements, resulting in dissolution of the anodic zones. If the cathodic sites are uniformly distributed at the beginning of the process, the attack will also be reasonably uniform at the beginning. As the anodic zones are eaten away, the cathodic zones would be expected to be dislodged from their places in the matrix metal and fall away from the workpiece. Under these conditions, the distribution of cathodic sites would remain fairly uniform and continuous smooth milling should result.

---

*R. B. Mears, J. Electrochem. Soc., <u>106</u>, (1959), p. 467.

On the other hand, if the cathodic zones are not uniformly distributed in the beginning, the milling rate will be higher on the matrix metal that is nearer to regions containing a high-density of cathodic activity. Similarly, the cathodic uniformity can change during milling, especially if the cathodic material tends to be dislodged from the surface in a spotty fashion (such as happens with Type 2219 alloy; see below).

Many other factors may be involved, of course. The anodic intensity may vary from point to point on the metal surface due to compositional differences in the aluminum matrix, caused perhaps by variations in the thermal history of the material at such points.

To summarize, uniform and smooth chemical milling of aluminum will result when the surface is uniformly covered with anodic and cathodic regions--both initially and during milling. These elements form a complex network of short-circuited cells, all with a common metallic path and a body of electrolyte that is also common to all cells. If anything develops that causes the average short-circuit current in any region to be appreciably different from that of another region, there will be a corresponding difference in the rate of attack in the two areas.

## B. The Etchant

The electrochemical features of the metal are quite important in determining chemical milling uniformity, but the electrolytic medium can also have a tremendous influence on the uniformity of attack. For example, an acidic medium and an alkaline medium can produce entirely different forms of attack on aluminum, even though the anode-cathode distribution of the metal is the same in both cases.

Similarly, alkaline solutions show different kinds of attack, depending on the presence of additives of various types. For example, addition of cyanide to a sodium hydroxide bath will change the relative potential between copper and aluminum to a smaller value than will be found in alkali alone, because copper ion forms a complex with cyanide ion that is soluble in alkali, whereas copper ion forms insoluble copper hydroxide in alkali alone.

When a copper-bearing aluminum alloy is chem-milled in alkali alone, the aluminum forms soluble sodium aluminate, but the copper remains as a finely divided black smut of metallic copper. This smut influences the rate of milling on the underlying aluminum, of course, since it prevents free access of fresh etchant to the surface. If some of the smut becomes detached in a given area, that area will suffer more rapid attack than will the smut-covered regions. In the presence of cyanide, however, the nature of the copper smut would be expected to be different than in alkali alone. At a high enough cyanide concentration the smut could be avoided entirely.

These remarks are intended to illustrate the possible influence of the etchant composition on the uniformity of attack on the aluminum alloy. Other variations in etchant composition could have similar effects--such effects being nearly impossible to predict merely from consideration of the chemical properties of the metals and etchant chemicals.

For example, the addition of sulfide to an alkaline etchant would not be expected to affect the solubility of aluminum in the medium--since aluminum does not form a stable sulfide--but it would considerably reduce the solubility of copper in the bath. Just how this influences the uniformity of attack on an aluminum surface is not easily predicted, however. All one can do is surmise that various bath additives could have an effect on smoothness and uniformity of stock removal, but in the end the determination of optimum bath compositions must be empirical.

In the present work, of course, the objective was to study the relationships between metallurgical factors and chem-milling properties, and was not concerned with a search for different milling compositions.

## VIII. SUMMARY AND RECOMMENDATIONS

### A. Type 2219 Aluminum

Nonuniform stock removal is caused by nonuniform quenching of the metal after solution treatment. The structural differences are noticeable between fast-etching and slow-etching areas; the former appear to have more precipitated material than the latter. While it is possible that etchant compositions could be discovered that would erase the metallurgical effects entirely, this seems quite remote because of the basic and inherent difference in the electrochemical structure of the fast and slow-quenched material. The slow-quenched alloy simply supports much more vigorous local action current when it is immersed in an alkaline etchant.

If the alloy must be chem-milled in the T37 temper, it would appear that a special grade of 2219-T37 alloy will have to be produced specifically for these applications. The quenching requirements could very probably be met by using a total immersion technique (vertical quenching) as opposed to the spray-quenching commonly used. It should be pointed out that the aluminum manufacturers have adopted spray quenching (in a horizontal position) because it is a much more economical and practical method for heat-treating large plates. The vertical method was formerly used, in fact, but was displaced by the more modern technique.

In all probability, the fabrication of Type 2219-T37 alloy can best be accomplished by mechanical milling methods, in view of the successful development of large-size equipment for this purpose.

B. Type 5456 Aluminum

It has been shown that the stretch marks that appear in this alloy are "electrochemically homogeneous" with the rest of the plate. That is, the marks are neither emphasized nor removed during chem-milling. If stretch marks are not acceptable in a given structure, they will simply have to be avoided in the first place.

The marks that appear on Type 5456 alloy are not, strictly speaking, "Luder" lines. Rather, they are more properly described as "Portevin-LeChatelier" markings, since they appear when the metal is stretched to a point near its ultimate strength. The term "Luder lines" refers to those marks that appear at the yield point of a metal. In the case of 5456, practically no banding occurs at the yield point.

C. Type 2014 Aluminum

The smoothness of chem-milling in this alloy is affected dramatically by the aging treatment. No variations in solution treatment or aging were discovered that significantly reduced the roughness that developed when the alloy was milled in the naturally aged condition. Furthermore, no direct correlations between the metallurgical structures of the metal in the two conditions of aging and their etching properties were discovered.

In this alloy particularly, the tendency for "electrochemical segregation" to occur during milling of the naturally aged material was marked. When the artificially aged alloy was milled, however, the distribution of anodic and cathodic zones appeared to remain constant with time, and smooth milling resulted.

A marked difference was discovered between the two lots of alloy studied. One lot showed a far greater etching difference between the two aging conditions than did the other lot. This is taken to be evidence that the composition of a nominal 2014 melt may vary sufficiently--and possibly in only one minor constituent--to cause marked differences in milling response. It is recommended, therefore, that chem-milling of Type 2014 alloy be done in the artificially aged state (T6), rather than in the "solution-treated and quenched" state (T4).

If fabrication methods demand that milling be done on metal in the T4 condition, it appears again that a "special milling grade" of Type 2014 alloy is a possibility. Such a composition could very probably be developed, since some lots of Type 2014 apparently already yield acceptable surfaces when milled in the T4 state.

### D. Type 7075 Aluminum

Roughness in this alloy is apparently also quite composition sensitive. No heat-treatment or aging variations were found that erased roughness completely in all samples of the alloy. There is a possibility, again, that a particular component of the alloy is chiefly responsible for rough milling, and that a statistical study of a number of lots of Type 7075 could identify the important element. It would then be possible to produce a "milling grade" alloy, as suggested earlier for 2219 and 2014.

Meanwhile, it would seem that a preliminary chem-milling test on small samples of the plate to be used would permit selection of those lots of material that would give acceptable surfaces.

## IX. LOGBOOKS AND CONTRIBUTING PERSONNEL

The data used in preparation of this report are recorded in IITRI Logbooks C15935, C16352, and C16705.

Personnel contributing to the guidance and execution of the experimental work were:

| | | |
|---|---|---|
| I. Broverman | - | Senior Metallurgist |
| F. A. Crossley | - | Senior Metallurgist |
| R. F. Dragen | - | Assistant Experimentalist |
| H. T. Francis | - | Manager, Electrochemistry |
| J. Kaminski | - | Technician |
| J. V. Smith | - | Chief Inspector, Gage Laboratory |

Respectfully submitted,

IIT RESEARCH INSTITUTE

Howard T. Francis

Howard T. Francis, Manager
Electrochemistry

Approved:

N. M. Parikh

N. M. Parikh, Director
Metals Research

HTF/fps